

NIPER-385
Distribution Category UC-122

SURFACTANT LOSS: EFFECTS OF TEMPERATURE,
SALINITY, AND WETTABILITY

Topical Report

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May 1989

Work Performed Under Cooperative Agreement No. FC22-83FE60149

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ABSTRACT

Adsorption of surfactants onto mineral surfaces has been studied as a function of temperature, solution salt concentration, and mineral surface wettability. Adsorption studies using a flow calorimeter were conducted using pure surfactants and minerals. The studies were then extended to the adsorption of one type of commercial surfactant onto both consolidated and crushed Berea sandstone using column techniques. This has allowed the comparison of different methods to evaluate surfactant losses from flowing rather than static surfactant solutions.

Molar enthalpy values measured during the calorimetry experiments indicated that adsorption was physical rather than chemical in nature. In general, adsorption decreased with an increase in temperature and increased as salinity increased, up to a maximum. These trends were consistent with an increase in adsorption associated with conditions which caused a decrease in surfactant solubility in solution.

Adsorption of one type of commercial surfactant having a high temperature and salinity tolerance was relatively constant over a temperature range of 24° to 90° C and salinity range of 5 to 15% NaCl. However, greater values of surfactant loss were measured under combined temperature and salinity conditions which caused surfactant precipitation. The magnitude of surfactant loss for crushed Berea was twice as great per gram of rock as the values measured for consolidated cores. Adsorption on oil-wet cores was up to 64% less than that on water-wet cores.

Evaluation of the importance of surfactant adsorption in an EOR project cannot neglect the effects of temperature, salinity, and surface properties. To a first approximation, changes in adsorption caused by changes in these parameters can be related to the way they affect or relate to surfactant solubility. Additional studies are required to determine the effects on adsorption which depend on the chemical nature of the surfactant.

INTRODUCTION

Chemical flooding is potentially one of the most versatile of all enhanced oil recovery techniques. Surfactant flooding has been shown to have high recovery efficiency but still is difficult to control in the field and usually requires high front-end investment costs. Considerable work has been published describing the techniques and requirements for formulating chemical slugs for various enhanced oil recovery (EOR) projects. These chemical slugs are often complex mixtures of surfactant, cosurfactant, and brine. Often a preflush is used to control salinity and divalent ion concentration. Adsorption, precipitation, or chromatographic separation of the components of such chemical treatment by reservoir minerals have been factors leading to loss of effectiveness and possible failure to recover incremental oil from the reservoir.

More than 200 fields and 900 formations in North America have reservoir temperatures that are greater than 170° F.¹ Major oil reservoirs in the North Sea, Alaska, and the U.S. Gulf Coast have temperatures that exceed 200° F and also have high salinities. Polymer and surfactant flooding are EOR methods that are being considered for application in deep, high-temperature reservoirs. Additional information regarding the behavior of surfactant systems at high temperatures is needed to establish procedures for optimizing chemical formulations for such applications.

The work described in this report is part of an overall program to evaluate and improve surfactant EOR methods. The emphasis in this area was the investigation of surfactant loss from flowing systems since static adsorption studies may not be representative of surfactant losses in the reservoir. The effects of temperature, salinity, and wettability on surfactant adsorption have been studied. The work was done using three separate dynamic adsorption methods: adsorption calorimetry, column adsorption studies, and core flooding experiments. Basic adsorption studies have been carried out by adsorption calorimetry, using high surface area minerals and pure surfactants dissolved in water or in brine. The basic work was related to column adsorption studies by running one of the mineral/surfactant combinations from the adsorption calorimetry in the column mode. The column work utilized crushed Berea sandstone to measure the surfactant loss of a commercial surfactant formulated for high-temperature, high-salinity conditions. Measurements of the extent of adsorption

of this surfactant on water-wet Berea and on oil-wet Berea cores completed the suite of determinations.

EXPERIMENTAL

During the course of this study, three different experimental apparatus were used to measure the effects of temperature, salinity, and wettability on the adsorption of surfactants from flowing systems. Adsorption of pure surfactants on mineral surfaces was measured using a flow calorimeter system to simultaneously monitor the amount and the heat of adsorption. Adsorption of commercial surfactants was measured by flowing surfactant solution through a column filled with crushed Berea sandstone. For experiments using consolidated cores, Berea cores were confined in a Hassler-sleeve pressurized core holder.

Materials

The solids used in the adsorption calorimeter were silica gel (SiO_2) and reverse phase silica ($\text{C}_{18}\text{SiO}_2$). The silica gel, a water-wet (hydrophilic) material, is Davison™ grade 62 silica gel. The reverse phase silica, an oil-wet (hydrophobic) material, was prepared from the above silica gel by refluxing it with octadecyl trichlorosilane in toluene, followed by treatment with methyl trichlorosilane. This procedure ensures that all the polar sites on the silica gel are converted to hydrophobic sites. The surfactants were anionic sodium dodecylsulfate (SDDS) from BDH Chemicals, Ltd., nonionic Triton™ X-100 (TR) from Rohm and Haas Co., and cationic decyltrimethylammonium bromide (DTAB) from Eastman Kodak Co.; all were used without further purification. Deionized water, which was then distilled from KMnO_4 , was used for all solutions. Sodium bromide (NaBr) was used as the electrolyte for the brine added to DTAB since it has a common ion with that surfactant. It was reagent grade obtained from Fisher Chemical Co. NaBr brine solutions were made up as 0.3, 0.6, and 0.9 molal, which are very nearly 3, 6, and 9% by weight, respectively. Further properties of these materials are listed in table 1.

For the column and core work, reagent grade sodium chloride (NaCl) was used to prepare the brines. Commercial EOR surfactants which were studied were carboxymethylated ethoxylated surfactants (CES). These were based on nonylphenol-(EO) $_n$ -carboxylates and were obtained from Chemische Werke Huls, AG. They were mixed thoroughly before use. The two CES samples contained an average

number of 5.5 and 6.5 EO groups per molecule, respectively. A higher average number of EO's results in greater water solubility of the surfactant. In addition, some non-ionizable material (up to 20%) may remain after conversion of the ethoxylates to the carboxymethylated ethoxylates. These surfactants have possible application in high-temperature, high-salinity environments. A previous NIPER report² describes some phase behavior studies with these surfactants to determine applicability to oil recovery processes.

The crushed Berea sandstone was prepared from the same block of sandstone as that used for the whole core experiments. The crushed samples were sieved, and columns were prepared from 180 to 212 mesh material. The measured surface area of the crushed material was 0.69 m²/g. This low value for the surface area suggests that the sample contained little clay.³

For experiments using consolidated cores, Berea sandstone was cut into 1.5 in. diameter by 4 in. cores. Some of these cores were used as the water-wet cores, while others were subjected to a wettability alteration procedure. The method selected for altering wettability of the cores was modified from a technique developed by Salter and Mohanty.⁴ In their work, the purpose was to obtain oil-wet cores for permeability studies, so the cores were initially fired to 1,600° F for 20 hours. Since the purpose of the current wettability alteration was to observe differences in adsorption losses due to water-wet versus oil-wet core, such high temperature initial firing of the cores was not appropriate.

In this study, the cores to be altered were heated to 110° C in a vacuum oven for 24 hours. They were transferred with minimum exposure to air into a glass reactor. In this unit, they were heated to 140° C for 6 hours, evacuated, and cooled to room temperature. The cores were then immersed in a 7% solution of dichlorodiphenylsilane in hexane and allowed to soak for a 72-hour period. The cores were placed in the vacuum oven and heated to 50° C for 24 hours. They were then returned to the reactor, where, using the same procedure, they were allowed to react with a 7% solution of chlorotrimethylsilane. This allowed conversion of polar sites which could not be contacted by the dichlorodiphenylsilane because of steric hindrance. Following another period in the vacuum oven as above, the cores were ready for flooding.

This wettability-alteration procedure was also applied to small cylindrical 3/4 x 1 in. plugs, which were used to evaluate the degree of wettability obtained from this alteration process. The wettability of four such plugs was determined using the USBM method.⁵ A USBM index of +1 indicates a highly water-wet surface while an index of -1 indicates a highly oil-wet surface. Table 2 shows the results of this test and indicates that all cores were altered to an oil-wet state, with an average value of -0.53. The average wettability value of untreated Berea core is 0.81.⁶

Adsorption Procedures

A typical adsorption experiment used the following general set of procedures. A series of surfactant solutions of increasing concentration was prepared in the solvent (water or brine) of interest. For the adsorption calorimeter, surfactant concentrations are reported as weight of surfactant/weight of solution. For the studies using commercial surfactants, concentrations are reported as weight of surfactant/volume of solution so that comparisons may be made with similar studies reported previously in the literature. Density measurements allow conversion from one concentration unit to the other.

The solvent was allowed to flow through the mineral sample to equilibrate the system. Care was taken to ensure that all the void volume in the system was filled with solution before introducing the first surfactant sample. The lowest concentration surfactant solution was then pumped through the system until the concentration of the produced fluid was equal to the concentration of the injected fluid. Surfactant concentration was monitored with either a refractive index or an ultraviolet detector. The next more concentrated solution was then pumped through the system. These steps were repeated until all solution concentrations were used. Solvent was then pumped through the sample to determine the amount of desorption, if any, that occurred.

Adsorption Calorimetry

Experimental methods using the LKB™ 2107-030 adsorption calorimeter followed the general method outlined above and have been described in more detail in previous reports.⁷⁻⁸ Changes in solution surfactant concentration during a run were monitored using a Knauer™ differential refractometer. This technique permits the

simultaneous measurement of the heat evolved and the extent of adsorption. A schematic diagram of the flow system is shown in figure 1.

A change was made in the previously reported procedure for loading the oil-wet reverse phase silica into the calorimeter in order to ensure that air was expelled from the cell and that fluid contacted the entire surface area of the solid. Since this material is completely hydrophobic, it is difficult for water to expel air from the surface and contact it satisfactorily. Five methods of initiating the experiment were compared by visual inspection and by checking the magnitude of the heat of adsorption of aqueous 1% SDDS solution. This concentration results in adsorption being in the plateau region (the region of maximum adsorption), and it provides a relatively large heat signal for comparison. After placing dry solid in the calorimeter, the methods which were used to fill the cell with liquids included:

1. Initiate water or brine flow through the system.
2. Draw a vacuum on the system before flowing water or brine.
3. Fill the calorimetry cell from the bottom with 75% aqueous isopropyl alcohol. Flow the alcohol solution for approximately 1 hour followed by overnight flow of water. If adsorption experiments used brine solutions, the system was flushed with brine for approximately 2 hours.
4. The same procedure as 3, only using pure acetone for the initial immersion.
5. Flow CO_2 gas through the system for 1 hour to replace the air, followed by overnight flow of water. The CO_2 is more soluble in water than is the air.

Methods 1 and 2 resulted in air pockets remaining in the solid. The system was not constructed to maintain a vacuum, so removal of air from the system using method 2 was not very efficient. Methods 3, 4, and 5 gave identical calorimetric results within experimental error; no air spaces were observed by visual inspection. The fact that method 5 provided the same results as those of 3 and 4 proved that the alcohol or acetone treatment did not alter the adsorption properties of the surface. For the experiments reported below, the initial filling with 75% isopropyl alcohol was used.

Values of the output concentrations needed to calculate the reduced surface excess for adsorption isotherms were determined by measuring the density of the

effluent solutions as described below under "Surfactant Analysis" for all solutions except those in 9% brine. The data for the latter solutions were obtained by the integration of the output of the differential refractometer, as previously described.⁸

Adsorption on Crushed Berea

The effects of temperature and salinity on adsorption of commercial surfactants were determined using chromatographic techniques. A schematic diagram of the liquid flow system is shown in figure 2. The system consists of a high-pressure liquid chromatographic pump, an adsorption column, and a differential refractometer to monitor changes in surfactant concentration. Crushed Berea sandstone (mesh 180 to 212) was packed into columns approximately 0.63 by 30.5 cm. The columns were saturated with NaCl brine, and the volume of each system from the injection port to the refractometer and to the outlet of the system was measured. After completing a typical experiment as described in "Adsorption Procedures", the amount of surfactant loss in the column was calculated from surfactant concentrations determined by one of several analytical methods as described in the "Surfactant Analysis" section below.

Adsorption on Consolidated Core

The experimental apparatus used for the consolidated core adsorption experiments was similar to that used for the crushed Berea studies; the basic difference being that a cylindrical core sample of 1.5 in. x 4 in. was used in place of the column of crushed core. The core was saturated prior to placing it in the core holder. A Hassler sleeve was used for applying overburden pressure. After assembling the core in the sleeve and core holder, the core was flooded with brine for 16 to 30 hours. Without this long equilibration period, a stable baseline could not be achieved for the UV detector at the start of the adsorption experiment.

After a stable baseline was obtained, a series of surfactant samples was introduced into the core. The principal differences between the consolidated core and the crushed core experiments were the larger pore volumes of the core and the longer times required for equilibration. The concentration of the effluent was determined by UV spectroscopy, as outlined under "Surfactant Analysis."

Calculation of Adsorption Isotherms

The amount of fluid entering and exiting the system was measured for the solvent and for each surfactant solution. The concentration of the injected solution is known from its preparation. The concentrations of the produced fluid were measured using one of the methods described below. At each step, the solution was pumped through the system until the concentration of the produced solution was equal to the concentration of the injected solution. Thus, the concentration of the injected solution became the "bulk concentration" for that step. By mass balance, the amount of surfactant and the amount of solvent remaining in the system after each step were determined; i.e., the difference between the amounts of the component entering and exiting the system during that step plus any amount of component already in the system at the beginning of the step. The adsorption, or more properly the surface excess amount of surfactant in the system, was calculated by one of the following equations, which are equivalent:

$$(g_2^\sigma)_i = \frac{1000 [(g_2)_i - v C_i]}{w} \quad (1a)$$

where g_2^σ is the mg of surfactant adsorbed/g rock; g_2 the grams of surfactant in the system; C is the concentration of surfactant, all at the end of step i ; v is the volume of the system, and w is the weight of the solid adsorbent in grams. For the flow calorimetry experiments, the surface excess amounts are given as follows:

$$(n_2^\sigma)_i = \frac{1000 [(n_2)_i - x_i(n_t)_i]}{w} \quad (1b)$$

where n_2^σ is the adsorption in mmol/g; n_2 is the number of moles of surfactant; x is the mole fraction of surfactant; and n_t is the total number of moles (solute + solvent) in the system at the end of step i . To facilitate the comparison of adsorption between surfaces, the amount adsorbed was normalized per square meter of surface, by dividing the adsorption in mmol/g by the specific surface area of the solid.

All of the excess surfactant was considered to be adsorbed on the mineral surface. Other processes which could cause surfactant losses, such as precipitation or decomposition, were not distinguished from adsorption losses to the solid.

A computer program to calculate the material balance equation has been developed previously for the adsorption calorimetry project.⁸ The program requires the amount and concentrations of the injected and produced solutions, the volume of the system, and the amount of adsorbent.

Surfactant Analysis

Several analytical methods were used to determine the surfactant concentrations in the output solutions. For solutions of pure surfactant containing up to 0.6 molal salt and for commercial surfactants with no salt, surfactant concentrations were determined using the density of the surfactant solutions. The densities were measured with a Sodev™ vibrating tube densimeter, sensitive to a few ppm. Correlations of density versus surfactant concentration for the pure surfactants are given in tables 3 through 6. In these tables, the apparent molar volume (V_ϕ) of the surfactant in solution is also given. The apparent molar volumes are calculated from:⁹

$$V_\phi = \frac{M}{d} - \frac{1000 (d - d^0)}{m d d^0} \quad (2)$$

where M is the molecular weight of the surfactant, d is the density of solution with molality m , and d^0 is the density of solvent. It should be noted that there is only a slight dependence of V_ϕ on surfactant concentration or on amount of electrolyte.

For surfactants containing a benzene ring in their structure, solution concentrations could also be determined using UV absorption. This was especially useful for the CES surfactants. The high salt concentration of the solutions did not interfere with the UV absorption of the surfactant. The CES molecule has a UV absorption peak at 283 nm. Figure 3 shows correlations between UV absorption and surfactant concentration for CES with 5.5 and 6.5 average ethoxylate groups, respectively. Output solutions in some cases required dilution to reduce surfactant concentration to the linear response range of these correlations. Therefore, the greatest accuracy using this method was obtained for solutions of low concentration that required no dilution before the measurement.

The third method for measuring the output solution concentrations used the response of the refractive index detector during the flow process to determine the relative amount of surfactant passing through or remaining in the system. This method could cause errors if the salt concentration varied as a result of contact with the solid,

because the refractive index detector responds to changes in salt concentrations as well as surfactant concentrations. In several cases, comparisons of adsorption calculations were made using concentrations determined using both the UV and RI methods.

RESULTS AND DISCUSSION

Adsorption Calorimetry

Adsorption Calorimetry as a Function of Surfactant Type and Temperature

The results of the adsorption calorimetry studies as a function of wettability, temperature, and surfactant type are presented in tables 8 through 17, and the enthalpy results are shown graphically in figures 4 through 7. The surface excess results are similar and have not been plotted. At the normal pH of the surfactant solutions, SiO_2 has a negative charge, so the anionic SDDS does not adsorb on it. Thus, there is no table for this combination of surfactant and mineral at either temperature. For each adsorption isotherm, there is a maximum adsorption, which is known as the adsorption plateau. To assist in comparing results, the plateau adsorption values are listed in table 18.

Several general trends can be noted in the adsorption results. First, the extent of adsorption decreased as the temperature increased, except for the case of the nonionic surfactant, TR, adsorbing on the oil-wet material. Second, for each surfactant type, adsorption was greater on the oil-wet surface than on the water-wet surface. A number of factors may contribute to the observed differences in adsorption on the two surfaces. These may include differences in adsorption sites on the two surfaces, differences in orientation of the surfactant on the surface, and differences in solvent/surface interactions.

Comparison can also be made of the relative adsorption of each surfactant type on one of the mineral surfaces. For the hydrophobic material at 25° C, the anionic had the highest adsorption, the cationic had less, and the nonionic the least of all. The relative order of the decrease in solubility for these surfactants is the same as the relative order of the increase in adsorption. Previous researchers have shown that within a specific surfactant type, adsorption increased with decreasing water solubility. Gale and Sandvik¹⁰ found that adsorption of petroleum sulfonate increased with increasing molecular weight and decreasing solubility. Lawson and Dilgren¹¹ and Trogus, et al.¹² found the same trend for the adsorption of alkylaryl sulfonates. Lawson and Dilgren¹¹ also found adsorption to increase with salinity in low salinity brines

which caused a decrease in surfactant solubility. Glover, et al.¹³ also found that adsorption of sulfonates increased with increasing salinity.

At 45° C, less difference was found in the adsorption values of the three surfactant types on C₁₈SiO₂. Once again, differences in solution properties, activity of the surfactant in solution, or changes in surfactant solubility may be affected by a change in solution temperature which, in turn, changes surfactant adsorption values.

Another general trend was that the molar enthalpy of adsorption for all surfactant types was greater (more exothermic) for the oil-wet material than for the silica. Adsorption is a complex process. The heat of adsorption represents the result of a displacement process in which the surfactant must compete with and displace the solvent (water) from the surface sites. The surfactant can more effectively compete with the solvent on the hydrophobic surface than on the water-wet surface. The measured heat should therefore represent the summation of the heat of surfactant removal from solution + the heat of solvent removal from the surface + the heat of surfactant adsorption on the surface. Comparison of the molar enthalpies for the two surfaces, therefore, would require some additional studies to evaluate the magnitude of the various heat effects during the adsorption process.

However, the quantity of heat indicates that this was physical adsorption (as contrasted with chemisorption). The molar enthalpy of hydrogen bonding in water is about -22 kJ/mol, compared to the present results which range from a low of -5 kJ/mol for the SiO₂-TR-25° combination to a high of -36 kJ/mol for the C₁₈SiO₂-DTAB-45° combination. In spite of the low enthalpy, the adsorption of these surfactants was, in general, irreversible.

The enthalpy of adsorption was exothermic, which suggests that the extent of adsorption should decrease with increasing temperature. In general, this was the case, with the exception of adsorption of the nonionic surfactant on the oil-wet surface. It must be remembered that the enthalpy of adsorption represents not just the attachment of surfactant on the surface, but also includes the process of taking it out of solution. Thus, the enthalpy of adsorption includes the solution properties of surfactants.

Adsorption of DTAB as a Function of Salinity and Temperature

To investigate the effects of salinity and temperature on the thermodynamics of adsorption, DTAB was selected as the surfactant since it adsorbs on both SiO_2 and $\text{C}_{18}\text{SiO}_2$. The electrolyte chosen was NaBr since it has a common ion with the surfactant. The concentrations of background electrolyte were 0, 0.3, 0.6, and 0.9 molal, which are very close to being 3, 6, and 9% by weight, respectively.

The results are given in tables 10, 11, 16, 17, and 19 to 30, and are shown in figures 8 through 11. Table 31 contains a summary of the plateau values. In general, the addition of salt increases the adsorption up to a maximum at 6% salt concentration. At 25° C, the adsorption at 9% is close to this plateau, while at 45° C it decreases, and in the case of the oil-wet material, it decreases dramatically. Also, the general trend is for the molar heat of adsorption to decrease with increasing salinity and to increase with temperature. The effects of temperature and salinity on adsorption seem to be opposed to each other.

The results of DTAB adsorption on reverse phase silica gel both with and without added salt can be fitted with a Langmuir isotherm. The Langmuir isotherm is sometimes incorporated into a process simulator to model adsorption processes. This isotherm is as follows:¹⁴

$$n_2^\sigma = \frac{n_m b C_2}{1 + b C_2} \quad (3)$$

where n_2^σ is the amount of surfactant adsorbed; C_2 is the surfactant solution concentration; n_m is a fitting parameter corresponding to monolayer adsorption on the surface; and b is a fitting parameter with units of reciprocal concentration corresponding to an equilibrium coefficient. The Langmuir equation can be rearranged in a linear form:

$$\frac{C_2}{n_2^\sigma} = \frac{C_2}{n_m} + \frac{1}{n_m b} \quad (4)$$

Thus, if the Langmuir equation provides an adequate description of the experiment, a plot of concentration divided by adsorption versus concentration will be a straight line, and is fitted to a straight line by the least-squares method. Table 32 lists the Langmuir parameters for adsorption of DTAB on reverse phase silica gel, and figures 12 and 13

show typical linear Langmuir plots. In table 32, the Langmuir parameter b has a value of 28 for 0.3 m NaBr background at 45° C, while it has a value of 267 for 0.6 m NaBr background at the same temperature. The corresponding values for n_m are 0.57 and 0.62 mmol/g, respectively. If one compares the top two curves in figure 11, which are for these same two conditions, one finds that the adsorption at the 0.6 m conditions reaches a higher plateau, corresponding to a larger n_m , and it reaches its plateau at a lower DTAB concentration than for the 0.3 m, corresponding to a larger b . This illustrates the meaning of the Langmuir parameters.

The Langmuir isotherm does not fit the adsorption of DTAB on SiO_2 because it has an S-shape. Woodbury and Noll have modeled¹⁵⁻¹⁷ the extent of adsorption and the enthalpy of adsorption. This model, which applies to Langmuir type isotherms as well as to S-shaped isotherms, uses a modified hemimicelle approach, but it incorporates the thermodynamic solution properties in a detailed manner. According to this model, adsorption above the CMC and the effects of temperature and added salt on adsorption rise mainly from changes in the solution properties of the surfactant – specifically, from changes in the activity of monomeric surfactant in solution.

Adsorption Using Column Equipment

Comparison With Previous Results

Several experiments were conducted to compare adsorption results from the adsorption calorimeter with those from the column adsorption apparatus. A column of the type used for the crushed Berea experiments was filled with SiO_2 and was used to measure the adsorption of DTAB at ambient temperatures. Results were compared with those obtained using the adsorption calorimeter. The only major difference in the experiments is that the SiO_2 sample size is approximately 10 times greater for the column apparatus than for the adsorption calorimeter. A comparison of results showed adsorption of DTAB agreed within 10%. Plateau adsorption using the adsorption calorimeter was 0.56 mmol/g, while using the column apparatus, it was 0.62 mmol/g.

Values for the adsorption of TR on crushed Berea can be found in the literature. Lawson¹⁸ published an adsorption value of 0.0013 g/m² using a sample of crushed Berea. In our column apparatus, an average value of 0.0010 g/m² \pm 20% was

determined. The surface area for Lawson's experiments was 1.2 m²/g compared to 0.69 m²/g for the sample used in this study.

CES Results

Adsorption of CES on crushed Berea core was measured at 24°, 50°, and 90° C for solutions containing 5, 10, and 15% NaCl. Adsorption loss from low concentration solutions was of primary interest so that surfactant concentrations of 0.05 and 0.1% were used for the first adsorption steps of the experiment. An additional step using 0.5% concentration solutions was run to assure that adsorption had reached the plateau or maximum level.

Effect of Temperature

The effect of temperature on the adsorption of the two CES samples in 5 and 10% NaCl brine is shown in tables 33 and 34. At 5% salt, there was a slight increase in adsorption with temperature. However, at 10% salt, temperature had little relative effect on the adsorption values for the 6.5 CES. Adsorption values were also similar for the 5.5 CES at 24° and 50° C. However, the amount of adsorption doubled at 90° C for this surfactant. In addition, desorption of the surfactant was minor except for the 5.5 CES at 90°C. Therefore, the adsorption values for CES at 50° C probably represent permanent surfactant losses to the rock.

The values obtained for adsorption at 50° C agree reasonably well with values reported by Balzar¹⁹ for adsorption of Hüls CES surfactants at 56° C on quartz. He measured values of 2.6 to 2.9 mg/m². For the crushed Berea sandstone used in this study, adsorption was 3.2 mg/m².

Adsorption is an exothermic process and should decrease as the temperature increases. This was observed in the adsorption studies using the adsorption calorimeter. Ziegler and Handy²⁰ observed that adsorption of a nonionic surfactant at very low concentrations decreased with increasing temperature. However, at high concentrations (above the CMC), adsorption increased with increasing temperature. They found that the rate of desorption also increased with increasing temperature.

The adsorption results for 5.5 CES at 90° C may begin to show some of these same trends as observed by Ziegler and Handy.²⁰ All surfactant concentrations used during this study were above the CMC. At high temperature, both adsorption and

desorption of the 5.5 CES appeared to increase significantly. For each experiment except the 5.5 at 90° C, most adsorption occurred out of the first or lowest concentration (0.05% CES) solution. However, for the adsorption of 5.5 CES at 90° C, half the total adsorption occurred out of the highest concentration solution (0.5% CES). These adsorption losses, however, were not irreversible as were observed for the other adsorption experiments at lower temperatures. More than 70% of the adsorbed surfactant redissolved in brine during the desorption step. Therefore, during an EOR project, useful surfactant concentrations may be available for oil mobilization from the desorption process.

In contrast, higher adsorption was not observed for 6.5 CES at 90° C. The increased average number of EO groups in the 6.5 CES increased its solubility in water. For surfactant solutions containing no oil, the 5.5 CES solution of sufficient surfactant concentration (above 0.1%) exhibited a cloud point close to 70° C. The cloud point of 6.5 CES was well above 90° C, however. With oil present, Olsen and Josephson² found that an increase of 1 in the EO number increased the phase inversion temperature by 30° C. Thus, at 90° C, the 5.5 CES is nearer to a phase inversion temperature than is the 6.5 material. This change in solubility with temperature may be related to the additional adsorption of the 5.5 and the absence of increased adsorption for the 6.5. It may be necessary to reach even higher temperatures before an increase in adsorption of 6.5 CES can be observed.

Effect of Salinity

The adsorption of 5.5 and 6.5 CES was also measured at 50° C as a function of changing salt concentrations. Table 35 shows a comparison of results for the two surfactants. The adsorption of 5.5 CES from 5 and 10% NaCl solutions was approximately the same. However, a dramatic increase in adsorption was observed for 5.5 CES in 15% brine. The cloud point of CES solutions is also a function of salinity. For 5.5 CES in 15% NaCl, the cloud point was approximately 45° C. Therefore, the solubility of the surfactant had been significantly reduced for this set of experimental conditions.

In contrast, a small increase in adsorption with an increase in salinity from 5 to 10% was observed for the 6.5 CES. No additional increase in adsorption was observed for surfactant solutions containing 15% salt. The higher solubility of the 6.5 CES resulted in little change in adsorption with increasing salinity. These

observations are similar to the effect of temperature on 6.5 CES adsorption. Additional experiments would be required to determine if high salinity at a temperature above 50° C would cause a significant increase in 6.5 CES surfactant adsorption.

In summary, adsorption for two carboxymethylated ethoxylated surfactants on crushed Berea sandstone remained approximately constant at 2 mg/g of rock (3 mg/m²) except for certain extreme conditions. For the 5.5 CES, adsorption increased at 50° C and 15% salinity and at 90° C and 10% salinity. These effects were not observed with 6.5 CES. The surfactant structure and resulting solution solubility should affect temperatures and salinities where increased adsorption may occur. Some indications exist, however, that these increased losses are reversible. Additional studies would be required to determine if these high surfactant losses would adversely affect EOR designs.

Adsorption Isotherms

The adsorption data for CES surfactants appear to be described adequately by the Langmuir isotherm (equations 3 and 4). Figure 14 shows the Langmuir fit for the 5.5 CES adsorption data at 50° and 90° C, while figure 15 shows the Langmuir fit for 6.5 CES under the same conditions. The plots for 6.5 CES at 50° and 90° C and that of the 5.5 at 50° C are typical examples for CES adsorption over the range of conditions investigated during this study. Maximum adsorption occurs at relatively low surfactant concentrations, and little additional adsorption occurs at the highest concentration (0.5%) used in this study.

The plot of 5.5 CES at 90° C represents the atypical situation where additional surfactant losses are observed in the crushed Berea sandstone experiment. The slope of this curve is much lower, and the intercept is much larger than the values for most other experimental conditions.

Table 36 lists the Langmuir constants n_m and b calculated from the slopes and intercepts of the Langmuir fits for 5.5 and 6.5 CES adsorption. Langmuir constants from these fits can be used in EOR simulators to design surfactant requirements for chemical floods. Within experimental error, n_m agrees with the maximum adsorption values reported in tables 33 through 35. The only major exception indicates that the adsorption of 5.5 CES at 90° C at very high solution concentration may be even higher than that reported in table 34.

The values of the Langmuir constant b for these concentration units are generally in the range of 20 to 50 (%)⁻¹. Very high values of b (greater than 100) are observed in cases where all the adsorption values used in the analysis are near or in the plateau adsorption region. Most or all of the adsorption has occurred at the lowest concentration solution. Once the adsorption sites on the solid surface have been satisfied, little additional adsorption occurs from the higher concentration solutions.

The one exception to these general results is the adsorption of 5.5 CES at 90° C. The Langmuir constant b is much lower for this case. This may represent some other type of surfactant loss that is occurring from this high-concentration solution.

Results of Adsorption On Consolidated Berea Core

Adsorption of both 5.5 and 6.5 EO CES on consolidated Berea cores was measured at 24°, 50° and 90° C for solutions containing 10% NaCl brine. The initial solution concentration used was 0.1 %, followed by a 0.5% concentration to ensure that adsorption had reached the plateau or maximum level.

The adsorption values for both the natural state, water-wet Berea cores and the treated, oil-wet cores are shown in table 37. Temperature increases had little relative effect on adsorption. For each experiment conducted, the majority of adsorption was observed from the lower, 0.1%, concentration CES solution. For both the 5.5 and 6.5 CES solutions at 90° C, all of the reported adsorption occurred from this lower concentration. Routine desorption experiments were not conducted using the consolidated core samples due to the increased times (up to 16 hours) required for the tests as compared with the crushed core experiments.

Water-Wet Cores

For the water-wet cores, an increase in temperature had little effect on the amount of adsorption at this brine concentration. Both the 5.5 and 6.5 series exhibited slightly higher adsorptions at 24° C, decreasing slightly at 50° and 90° C. The adsorption value for the 5.5 EO material is more than that for the 6.5 at each temperature.

The adsorption values obtained at the various temperatures compare well with those reported by Balzar¹⁹ and with those conducted using crushed Berea. An overall

comparison of adsorption values for the consolidated/crushed Berea indicates that there was approximately 50% less adsorption for the consolidated core at a given temperature and salt concentration. It is expected that consolidated core adsorption values should be less than those for the crushed core experiments, since additional surface is created by the crushing process, no matter how carefully the core is disaggregated. A comparison of adsorption per unit area for the consolidated versus crushed Berea is unavailable as our surface area analyzer requires disaggregation of the sample to determine the surface area.

Oil-Wet Cores

Adsorption of the 5.5 and 6.5 CES was evaluated at 24°, 50° and 90° C using the altered cores. Results are given in table 37. Adsorption values were consistently lower for the oil-wet core as compared to the unaltered core at the same conditions. However, the adsorption of surfactant increased with each temperature increase for the oil-wet system. The adsorption value of the 5.5 CES increased 67% in going from 24° to 50° C, and increased another 21% in going to 90° C. In like manner, the 6.5 CES adsorption increased 25% from 50° to 90° C.

In comparison to the unaltered core, the adsorption values for the oil-wet cores were lower by 64% for the 5.5 CES at 24° C. Likewise, at 50° C the adsorption values were lower by 28% for the 5.5 CES and 31% for the 6.5. At 90° C, only a 13% difference in adsorption values for the water-wet and oil-wet cores was observed for each CES series. These trends can be compared with the adsorption of DTAB on water-wet and oil-wet surfaces in the presence of salt. For the DTAB, adsorption on the oil-wet surface was lower than that on the water-wet surface, and the difference in adsorption on the two surfaces was less at the higher experimental temperature.

SUMMARY

Adsorption of surfactants on mineral surfaces has been studied as a function of temperature, salinity, and wettability of the mineral surface. The adsorption of pure surfactants (SDDS, DTAB, and TR) and one type of commercial surfactant (CES) has been measured during this year as part of BE4A, tasks 2 and 3 of DOE's base program at NIPER. Adsorption was measured from flowing solutions on both consolidated and unconsolidated mineral surfaces. Comparisons were made between adsorption results measured for the different types of mineral surfaces. Comparisons were also

made for adsorption on pure minerals such as silica gel (SiO_2) and on crushed and consolidated Berea sandstone cores.

Adsorption calorimetric studies using pure minerals and surfactants indicated that the extent of adsorption tended to decrease with increasing temperature and increase with increasing salt concentration, up to a maximum at 6% brine. At 45° C, the extent of adsorption decreased when the brine concentration went from 6 to 9% for pure cationic surfactant on both the water-wet SiO_2 and the oil-wet reverse phase silica gel ($\text{C}_{18}\text{SiO}_2$). The molar enthalpy of adsorption of this surfactant on these surfaces increased with increasing temperature and decreased with increasing brine concentration. Brine concentration and temperature both affected surfactant behavior in solution and may have opposing influences on surfactant losses during chemical flooding operations. The chemical nature of the surfactant was also an important factor in determining the magnitude of the competing forces in a specified situation.

Comparison of adsorption results for treated and untreated SiO_2 showed that adsorption was generally lower on an oil-wet surface at ambient temperatures and in the presence of salt in solution. As the temperature increased, however, differences in adsorption on the two surfaces diminished. With no salt in solution, adsorption was greater on an oil-wet surface for all types of surfactants tested (cationic, anionic, and non-ionic). The molar enthalpy of adsorption was greater for the oil-wet surface than for the water-wet system at any given combination of temperature and salinity.

For studies using crushed Berea sandstone and a commercial surfactant (carboxymethylated ethoxylated surfactant, CES), adsorption varied only slightly with temperatures up to 50° C and salinities up to 10% NaCl. This adsorption appeared to be irreversible. At 90° C, adsorption approximately doubled. This increase in adsorption, however, did not represent an irreversible surfactant loss to the reservoir. Subsequent flow of brine reduced adsorption losses to levels comparable with those at 50° and 24° C.

A comparison of surfactant adsorption on oil-wet and water-wet Berea cores indicated that adsorption of CES in a 10% brine varied little at 24°, 50°, and 90° C. Less CES was adsorbed on the oil-wet core at each temperature evaluated. However, there was a noted increase in the amount of adsorption for the oil-wet core for each increase in temperature, whereas the adsorption values for the water-wet core remained essentially constant as temperature increased.

Less adsorption per gram of rock was observed for consolidated Berea sandstone as compared with the unconsolidated sandstone. This result would be consistent with the lower specific surface area exposed to surfactant solution in the consolidated core.

In conclusion, surfactant adsorption from flowing systems has been measured using three different techniques that measure surfactant losses on consolidated and unconsolidated mineral surfaces. Temperature, salinity, and the nature of the mineral surface can all influence the amount of surfactant loss to the reservoir. The trends observed with one variable may be offset by the influence of the other variables on adsorption. The nature of the surfactant has an effect on the observed influence of these parameters. These parameters can affect solution properties and solubility of the surfactant. Additional studies would be required to further define these influences on surfactant adsorption.

CONCLUSIONS

Adsorption Calorimetry: Pure Surfactants and Minerals

- In general, factors which decrease surfactant solubility increase adsorption.
- Adsorption decreases with an increase in temperature, except for adsorption of a nonionic surfactant on oil-wet material.
- Adsorption increases up to a maximum with increasing salt concentration.
- Temperature, salinity, and wettability may have opposing effects on surfactant adsorption.
- Adsorption of an ionic surfactant on an oil-wet surface is greater than adsorption on a water-wet surface under no salt conditions. However, the presence of salt in solution results in higher adsorption on the water-wet surface. As the temperature increases in the presence of salt, the amount of adsorption on the water-wet and oil-wet surfaces becomes more similar.
- The magnitude of the molar enthalpy of adsorption indicates that surfactant adsorption is a physical and not a chemical process.

- In general, molar enthalpies of adsorption decrease with increasing salt concentration. These enthalpies represent a combination of processes, including the enthalpy of surfactant in solution (solution properties) as well as the enthalpy of surfactant on the solid surface.
- Molar enthalpies of adsorption are higher for adsorption on the oil-wet material than the corresponding adsorption on the water-wet material. This suggests that adsorption calorimetry with a probe molecule may be a useful method for determining wettability of reservoir rocks.
- An adsorption model has been developed which attributes the effects of added salt on the extent of adsorption to changes in monomeric surfactant activity.
- Adsorption of nonionic surfactant is affected least by changes in temperature and surface wettability (effect of salt was not studied) as compared with the adsorption of ionic surfactants.

Column Adsorption: Commercial Surfactant

- Commercial surfactants, CES, with high temperature and salinity tolerance have relatively constant adsorption characteristics over a wide range of salt concentrations and temperatures.
- Results of CES adsorption studies using crushed and consolidated Berea cores are similar. However, the magnitude of adsorption per gram of solid is greater for crushed Berea sandstone. This is consistent with a greater specific surface area for the crushed Berea compared with the consolidated Berea core.
- Adsorption trends of CES with temperature and salinity compare more closely to those of nonionic pure surfactants than those of ionic surfactants. CES is a mixture of 80% anionic and 20% nonionic surfactants. Therefore, the nonionic surfactant is influencing the adsorption characteristics of the mixture.

Adsorption From Consolidated Core: Commercial Surfactant

- Less adsorption on a mass basis was noted by consolidated cores than by unconsolidated Berea sandstone.

- Adsorption values for the consolidated water-wet Berea were higher for the 5.5 CES as compared with the 6.5 CES at all temperatures tested.
- Less adsorption was noted for an oil-wet consolidated Berea core than was found for a water-wet core. However, adsorption values for the oil-wet core increased with each increase in temperature while adsorption values for a consolidated water-wet Berea core decreased slightly as temperature increased from 24° to 90° C for both CES series.

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TABLE 1. - Surfactants and minerals for adsorption experiments

Name	Abbreviation	Type	Molecular weight Daltons
<u>Surfactants</u>			
Decyltrimethylammonium bromide	DTAB	cationic	280.3
Triton™ X-100	TR	nonionic	620
Sodium dodecylsulfate	SDDS	anionic	288.4
Carboxymethylated ethoxylates	CES	80% anionic/ 20% nonionic	542 to 586
Name	Abbreviation	Surface area m ² /g	
<u>Minerals</u>			
Silica gel	SiO ₂	330	
Reverse phase silica gel	C ₁₈ SiO ₂	269	
Crushed Berea sandstone		0.69	

TABLE 2. - Wettability values for altered cores

Core	Wettability value ¹
1	-0.28
2	-0.82
3	-0.35
4	-0.68

¹Scale: -1=highly oil-wet, +1=highly water-wet

TABLE 3. - Density of aqueous SDDS at 25° C

Mass %	Molality mol/kg	Density g/mL	V_{ϕ} mL/mol
0	0	0.997062	---
0.2500	0.008691	0.997474	241.4
0.5000	0.01742	0.997814	245.6
0.7500	0.02620	0.998151	247.2
1.000	0.03503	0.998486	248.0
1.500	0.05280	0.999137	249.2
1.976	0.06990	0.999769	250.0
3.000	0.1072	1.001133	250.0
3.903	0.1408	1.002330	250.3

TABLE 4. - Density of aqueous TR at 25° C

Mass %	Molality mol/kg	Density g/mL	V_{ϕ} mL/mol
0	0	0.997062	---
0.2500	0.004042	0.997293	564.2
0.5000	0.008105	0.997501	567.1
0.7500	0.01219	0.997746	565.0
1.000	0.01629	0.997929	567.8
1.250	0.02042	0.998147	567.8
1.500	0.02456	0.998360	567.9
1.750	0.02873	0.998578	567.9
2.000	0.03292	0.998783	568.3
2.500	0.04136	0.999216	568.2
3.000	0.04988	0.999664	567.9
3.500	0.05850	1.000090	568.0
4.000	0.06720	1.000522	568.1

TABLE 5. - Density of aqueous DTAB at 25° C

Mass %	Molality mol/kg	Density g/mL	V_ϕ mL/mol
0	0	0.997062	---
0.2500	0.008942	0.997266	258.1
0.5000	0.01793	0.997477	257.7
0.7500	0.02696	0.997682	257.8
1.000	0.03604	0.997890	257.8
1.250	0.04516	0.998102	257.7
1.500	0.05433	0.998307	257.8
1.750	0.06355	0.998514	257.8
2.000	0.07281	0.998695	258.1
2.500	0.09148	0.999025	259.0
3.000	0.1103	0.999352	259.7
3.500	0.1294	0.999682	260.0
4.000	0.1486	1.000011	260.4

TABLE 6. - Density of DTAB in 0.3 m NaBr at 25° C

Mass %	Molality mol/kg	Density g/mL	V_ϕ mL/mol
0	0	1.020256	---
0.2496	0.008927	1.020442	254.7
0.4998	0.01792	1.020531	259.9
0.7499	0.02696	1.020657	260.3
0.9663	0.03481	1.020772	260.4
1.499	0.05430	1.021011	261.2
2.000	0.07281	1.021247	261.4
2.999	0.1103	1.021697	261.8
3.999	0.1486	1.022177	261.8

TABLE 7. - Density of DTAB in 0.6 m NaBr at 25° C

Mass %	Molality mol/kg	Density g/mL	V_ϕ mL/mol
0	0	1.042847	---
0.2499	0.008938	1.042878	265.6
0.5000	0.01793	1.043019	259.9
0.7490	0.02692	1.043194	256.8
0.9998	0.03603	1.043256	258.2
1.500	0.05433	1.043570	256.4
1.994	0.07259	1.043450	261.0
3.000	0.1103	1.043758	261.0
3.994	0.1484	1.044026	261.2

TABLE 8. - Adsorption calorimetry of TR on SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
1.100	-3.36	-10.2	0.68	2.06	-4.9
2.200	-3.36	-10.2	0.68	2.07	-4.9
3.300	-3.36	-10.2	0.68	2.07	-4.9
4.300	-3.36	-10.2	0.68	2.07	-4.9

TABLE 9. - Adsorption calorimetry of TR on SiO₂ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-2.51	-7.6	0.40	1.21	-6.3
0.5000	-2.51	-7.6	0.41	1.24	-6.1
1.000	-2.51	-7.6	0.44	1.33	-5.7
1.996	-2.51	-7.6	0.47	1.42	-5.3
4.000	2.51	-7.6	0.47	1.42	-5.3

TABLE 10. - Adsorption calorimetry of DTAB in distilled water on SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-1.04	-3.2	0.05	0.15	-20.0
0.5000	-1.27	-3.8	0.07	0.22	-17.0
0.7500	-1.45	-4.4	0.10	0.30	-14.5
1.000	-1.59	-4.8	0.12	0.36	-13.2
1.250	-1.72	-5.2	0.15	0.45	-11.5
1.500	-1.85	-5.6	0.18	0.55	-10.2
1.750	-2.14	-6.5	0.28	0.85	-7.6
2.000	-2.72	-8.2	0.40	1.21	-6.8
2.500	-3.12	-9.5	0.49	1.48	-6.4
3.000	-3.33	-10.1	0.54	1.64	-6.2
3.500	-3.47	-10.5	0.56	1.70	-6.2
4.000	-3.57	-10.8	0.58	1.76	-6.2

TABLE 11. - Adsorption calorimetry of DTAB in distilled water on SiO₂ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.5130	-1.22	-3.7	0.02	0.061	-61
0.9380	-1.40	-4.2	0.03	0.097	-43
1.490	-1.64	-5.0	0.05	0.16	-31
1.880	-2.34	-7.1	0.11	0.33	-21
2.420	-3.05	-9.2	0.19	0.58	-16
2.850	-3.25	-9.8	0.21	0.64	-15
3.690	-3.47	-10.5	0.24	0.73	-15

TABLE 12. - Adsorption calorimetry of SDDS on C₁₈SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-11.8	-44.0	0.66	2.45	-18.0
0.5000	-12.0	-44.8	0.70	2.59	-17.3
1.000	-12.2	-45.4	0.70	2.61	-17.4
2.000	-12.4	-46.2	0.69	2.58	-17.9
4.000	-12.7	-47.2	0.68	2.53	-18.4

TABLE 13. - Adsorption calorimetry of SDDS on C₁₈SiO₂ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-18.0	-66.9	0.56	2.09	-32.0
0.5000	-18.4	-68.5	0.58	2.17	-31.6
0.7500	-18.5	-68.8	0.58	2.17	-31.7
1.000	-18.6	-69.1	0.58	2.17	-31.8
2.000	-18.8	-69.9	0.58	2.16	-31.9
4.000	-19.2	-71.4	0.58	2.16	-33.0

TABLE 14. - Adsorption calorimetry of TR on C₁₈SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-7.33	-27.4	0.40	1.49	-18.4
0.5000	-7.39	-27.6	0.39	1.46	-18.7
0.7500	-7.39	-27.6	0.39	1.46	-18.7
1.000	-7.39	-27.6	0.39	1.46	-18.7
1.878	-7.39	-27.6	0.39	1.46	-18.7
4.000	-7.39	-27.6	0.39	1.46	-18.7

TABLE 15. - Adsorption calorimetry of TR on C₁₈SiO₂ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-8.57	-31.9	0.43	1.60	-19.9
0.5000	-8.57	-31.9	0.44	1.64	-19.4
0.7500	-8.57	-31.9	0.44	1.64	-19.4
1.000	-8.57	-31.9	0.44	1.64	-19.4
1.878	-8.57	-31.9	0.44	1.64	-19.4
4.000	-8.57	-31.9	0.44	1.64	-19.4

TABLE 16. - Adsorption calorimetry of DTAB in distilled water on C₁₈SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-4.95	-18.5	0.24	0.89	-21.0
0.5000	-6.79	-25.3	0.32	1.20	-21.1
0.7500	-7.94	-29.6	0.38	1.41	-21.1
1.000	-8.76	-32.7	0.41	1.52	-21.5
1.250	-9.42	-35.1	0.44	1.64	-21.4
1.500	-9.98	-37.2	0.47	1.76	-21.1
1.750	-10.4	-39.0	0.52	1.93	-20.2
2.000	-10.6	-39.9	0.54	2.03	-19.7
3.000	-10.8	-40.3	0.55	2.05	-19.7
3.916	-10.8	-40.4	0.57	2.12	-19.1

TABLE 17. - Adsorption calorimetry of DTAB in distilled water on $C_{18}SiO_2$ at 45° C

Mass %	Enthalpy of adsorption J/g	Enthalpy of adsorption mJ/m ²	Surface mmol/g	Surface excess $\mu\text{mol/m}^2$	Molar enthalpy kJ/mol
0.2500	-5.98	-22.2	0.20	0.74	-29.9
0.5000	-8.56	-31.8	0.28	1.05	-30.2
0.7500	-10.17	-37.8	0.33	1.22	-30.9
1.000	-11.4	-42.3	0.36	1.35	-31.4
1.250	-12.3	-45.8	0.39	1.45	-31.6
1.500	-13.1	-48.8	0.39	1.46	-33.4
1.750	-13.8	-51.3	0.40	1.49	-34.4
2.000	-14.2	-52.9	0.40	1.50	-35.2
2.500	-14.4	-53.6	0.40	1.50	-35.6
3.000	-14.5	-53.8	0.40	1.50	-35.8
3.500	-14.5	-53.9	0.40	1.50	-35.9
4.000	-14.5	-54.1	0.40	1.50	-35.9

TABLE 18. - Plateau values for adsorption calorimetry of SDDS, TR and DTAB from water on water-wet and oil-wet materials

Mineral	Temp. °C	Surfactant	Enthalpy mJ/m ²	Surface excess $\mu\text{mol/m}^2$	molar enthalpy kJ/mol
$C_{18}SiO_2$	25	SDDS	-47.2	2.53	-18.4
$C_{18}SiO_2$	45	SDDS	-71.4	2.16	-33.0
SiO_2	25	TR	-10.2	2.07	-4.9
SiO_2	45	TR	-7.6	1.42	-5.3
$C_{18}SiO_2$	25	TR	-27.6	1.49	-18.7
$C_{18}SiO_2$	45	TR	-31.9	1.64	-19.4
SiO_2	25	DTAB	-10.8	1.76	-6.2
SiO_2	45	DTAB	-10.5	0.73	-14.6
$C_{18}SiO_2$	25	DTAB	-40.4	2.12	-19.1
$C_{18}SiO_2$	45	DTAB	-54.1	1.50	-35.9

TABLE 19. - Adsorption calorimetry of DTAB in 0.3 m NaBr on SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-1.19	-3.6	0.06	0.18	-19.8
0.5000	-2.19	-6.6	0.22	0.67	-10.0
0.7500	-4.29	-13.0	0.85	2.58	-5.0
1.000	-4.55	-13.8	0.91	2.76	-5.0
1.250	-4.66	-14.1	0.94	2.85	-5.0
1.500	-4.73	-14.3	0.97	2.94	-4.9
1.750	-4.81	-14.6	1.00	3.03	-4.8
2.000	-4.89	-14.8	1.02	3.09	-4.8
2.500	-4.96	-15.0	1.03	3.12	-4.8
3.000	-5.02	-15.2	1.03	3.12	-4.8
3.500	-5.07	-15.4	1.03	3.12	-4.8
4.000	-5.11	-15.5	1.03	3.12	-4.8

TABLE 20. - Adsorption calorimetry of DTAB in 0.6 m NaBr on SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-1.36	-4.1	0.09	0.28	-15.1
0.5000	-4.93	-14.9	0.95	2.88	-5.2
0.7500	-5.20	-15.8	1.02	3.09	-5.1
1.000	-5.30	-16.1	1.06	3.21	-5.1
1.250	-5.36	-16.2	1.07	3.24	-5.0
1.500	-5.43	-16.4	1.08	3.27	-5.0
1.750	-5.46	-16.5	1.09	3.30	-5.0
2.000	-5.46	-16.5	1.09	3.30	-5.0
2.500	-5.47	-16.6	1.09	3.30	-5.0
3.000	-5.48	-16.6	1.09	3.30	-5.0
3.500	-5.48	-16.6	1.09	3.30	-5.0
4.000	-5.48	-16.6	1.09	3.30	-5.0

TABLE 21. - Adsorption calorimetry of DTAB in 0.9 m NaBr on SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-2.55	-7.7	0.27	0.82	-9.4
0.5000	-5.10	-15.5	0.96	2.91	-5.3
0.7500	-5.24	-15.9	1.10	3.33	-4.8
1.000	-5.30	-16.1	1.10	3.33	-4.9
1.250	-5.34	-16.2	1.10	3.33	-4.9
1.500	-5.35	-16.2	1.10	3.33	-4.9
1.750	-5.35	-16.2	1.10	3.33	-4.9
4.000	-5.35	-16.2	1.10	3.33	-4.9

TABLE 22. - Adsorption calorimetry of DTAB in 0.3 m NaBr on SiO₂ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2453	-0.70	-2.1	0.02	0.061	-35
0.4937	-1.32	-4.0	0.05	0.15	-26
0.7337	-4.95	-15.0	0.40	1.21	-12.4
0.9965	-5.68	-17.2	0.52	1.58	-10.9
1.500	-5.93	-18.0	0.59	1.79	-10.0
2.050	-6.06	-18.4	0.61	1.85	-9.9
3.000	-6.15	-18.6	0.63	1.91	-9.8
3.500	-6.20	-18.8	0.65	1.97	-9.5
4.000	-6.20	-18.8	0.65	1.97	-9.5

TABLE 23. - Adsorption calorimetry of DTAB in 0.6 m NaBr on SiO₂ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-0.70	-2.1	0.04	0.12	-17.0
0.5000	-7.00	-21.2	0.59	1.79	-11.9
0.7500	-7.64	-23.2	0.71	2.15	-10.7
1.000	-7.78	-23.6	0.74	2.24	-10.5
1.500	-7.92	-24.0	0.75	2.27	-10.6
2.000	-7.97	-24.2	0.75	2.27	-10.6
4.000	-7.97	-24.2	0.75	2.27	-10.6

TABLE 24. - Adsorption calorimetry of DTAB in 0.9 m NaBr on SiO₂ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-1.25	-3.8	0.06	0.18	-20.8
0.5000	-6.75	-20.5	0.78	2.36	-8.7
0.7500	-6.96	-21.1	0.83	2.52	-8.4
1.000	-7.05	-21.4	0.85	2.58	-8.3
1.500	-7.12	-21.6	0.86	2.61	-8.3
2.000	-7.18	-21.8	0.86	2.61	-8.3
4.000	-7.18	-21.8	0.86	2.61	-8.3

TABLE 25. - Adsorption calorimetry of DTAB in 0.3 m NaBr on C₁₈SiO₂ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-9.5	-35.3	0.53	1.99	-17.7
0.4999	-10.6	-39.7	0.61	2.27	-17.5
0.7500	-11.2	-41.6	0.64	2.40	-13.3
0.9996	-11.2	-41.9	0.64	2.37	-17.6
2.000	-11.3	-42.1	0.64	2.37	-17.6
4.000	-11.3	-42.2	0.64	2.37	-17.6

TABLE 26. - Adsorption calorimetry of DTAB in 0.6 m NaBr on $C_{18}SiO_2$ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2500	-10.2	-37.8	0.59	2.20	-17.2
0.5000	-11.1	-41.4	0.66	2.46	-16.8
0.7500	-11.2	-41.6	0.66	2.46	-16.9
1.000	-11.2	-41.7	0.66	2.45	-16.9
2.000	-11.2	-41.7	0.66	2.45	-16.9
4.000	-11.2	-41.7	0.66	2.45	-16.9

TABLE 27. - Adsorption calorimetry of DTAB in 0.9 m NaBr on $C_{18}SiO_2$ at 25° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2483	-10.7	-39.8	0.62	2.32	-17.2
0.4950	-11.1	-41.4	0.66	2.46	-16.7
1.000	-11.2	-41.5	0.64	2.39	-17.3
2.000	-11.2	-41.6	0.64	2.38	-17.3
4.000	-11.2	-41.6	0.64	2.38	-17.3

TABLE 28. - Adsorption calorimetry of DTAB in 0.3 m NaBr on $C_{18}SiO_2$ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2496	-12.7	-47.2	0.44	1.64	-28.9
0.4998	-14.4	-53.5	0.51	1.89	-28.3
0.7499	-15.5	-57.6	0.56	2.07	-27.8
0.9663	-15.6	-58.0	0.56	2.07	-28.0
1.4993	-15.6	-58.0	0.56	2.07	-28.0
2.000	-15.6	-58.0	0.56	2.07	-28.0
3.999	-15.6	-58.0	0.56	2.07	-28.0

TABLE 29. - Adsorption calorimetry of DTAB in 0.6 m NaBr on $C_{18}SiO_2$ at 45° C

Mass %	Enthalpy of adsorption		Surface excess		Molar enthalpy
	J/g	mJ/m ²	mmol/g	μmol/m ²	kJ/mol
0.2496	-14.6	-54.3	0.55	2.04	-26.6
0.5000	-16.4	-61.0	0.65	2.42	-25.1
0.7490	-16.5	-61.3	0.62	2.31	-25.5
0.9980	-16.5	-61.3	0.62	2.31	-25.5
1.994	-16.6	-61.7	0.62	2.31	-25.5
3.994	-16.6	-61.7	0.62	2.31	-25.5

TABLE 30. - Adsorption calorimetry of DTAB in 0.9 m NaBr on $C_{18}SiO_2$ at 45° C

Mass %	Enthalpy of adsorption J/g	Enthalpy of adsorption mJ/m ²	Surface excess mmol/g	Surface excess μ mol/m ²	Molar enthalpy kJ/mol
0.2500	-10.8	-40.1	0.43	1.61	-24.9
0.5000	-11.8	-43.9	0.50	1.85	-23.7
0.7500	-12.0	-44.6	0.50	1.85	-24.0
1.000	-12.0	-44.6	0.50	1.85	-24.0
4.000	-12.0	-44.6	0.50	1.85	-24.0

TABLE 31. - Plateau values for adsorption calorimetry of DTAB as a function of temperature and salinity on water-wet and oil-wet materials

Solid	Temp °C	Brine concentration molality	Enthalpy mJ/m ²	Surface excess μ mol/m ²	Molar enthalpy kJ/mol
SiO ₂	25	0	-10.8	1.76	-6.2
		0.3	-15.5	3.12	-4.8
		0.6	-16.6	3.30	-5.0
		0.9	-16.2	3.33	-4.9
	45	0	-10.5	0.73	-14.6
		0.3	-18.8	1.97	-9.4
		0.6	-24.2	2.27	-10.6
		0.9	-21.8	2.61	-8.3
$C_{18}SiO_2$	25	0	-40.4	2.12	-19.1
		0.3	-42.2	2.37	-17.6
		0.6	-41.7	2.45	-17.0
		0.9	-41.6	2.38	-17.3
	45	0	-54.1	1.50	-35.9
		0.3	-58.0	2.07	-28.0
		0.6	-61.7	2.31	-25.5
		0.9	-44.6	1.85	-24.0

TABLE 32. - Langmuir parameters for adsorption of DTAB on C₁₈SiO₂

Temperature °C	Salinity m	n _m mmol/g	b (%) ⁻¹
25	0	0.63	2
	0.3	0.64	40
	0.6	0.66	100
	0.9	0.64	300
45	0	0.43	5
	0.3	0.57	28
	0.6	0.62	267
	0.9	0.50	71

TABLE 33. - Adsorption of CES in 5% NaCl on crushed Berea sandstone as a function of temperature

Surfactant	Temperature °C	Adsorption mg/g	Desorption %
5.5 CES	24	1.8	0
	50	2.1	2
6.5 CES	24	1.4	3
	50	1.7	0

TABLE 34. - Adsorption of CES in 10% NaCl on crushed Berea as a function of temperature

Surfactant	Temperature °C	Adsorption mg/g	Desorption %
5.5 CES	24	1.9	2
	50	2.1	3
	90	5.2	76
6.5 CES	24	1.8	2
	50	2.1	7
	90	2.1	0

TABLE 35. - Adsorption of CES at 50° C on crushed Berea as a function of salinity

Surfactant	Salinity % NaCl	Adsorption mg/g	Desorption %
5.5 CES	5	1.9	3
	10	2.1	3
	15	6.2	*
6.5 CES	5	1.3	0
	10	2.1	7
	15	1.9	12

* Desorption was not measured.

TABLE 36. - Langmuir parameters for the adsorption of CES on crushed Berea sandstone

EO	Salinity % NaCl	Temp. ° C	n_m mg/g	b (%) ⁻¹
5.5	5	24	1.8	40
	5	50	2.1	120
	10	24	2.0	40
	10	50	2.1	3900
	10	90	7.5	4
6.5	5	24	1.5	50
	5	50	2.0	40
	10	24	2.0	20
	10	50	2.2	50
	10	90	2.3	20

TABLE 37. - Adsorption of CES in 10% NaCl on consolidated Berea cores

Surfactant	Temperature °C	Adsorption on water-wet core mg/g	Adsorption on oil-wet core mg/g
5.5 CES	24	1.2	0.43
	50	1.0	0.72
	90	1.0	0.87
6.5 CES	24	0.88	---
	50	0.84	0.58
	90	0.84	0.73

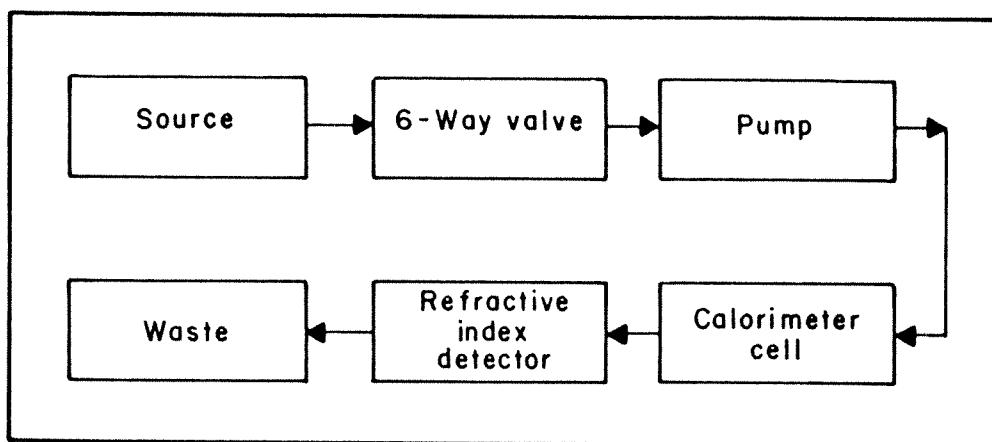


FIGURE 1. - Schematic diagram of the flow adsorption calorimeter system.

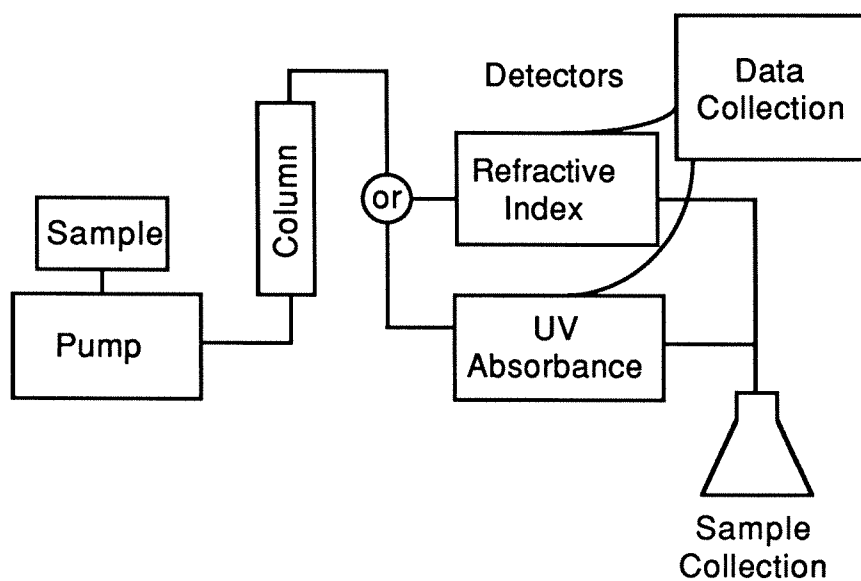


FIGURE 2. - Schematic diagram of the column adsorption system.

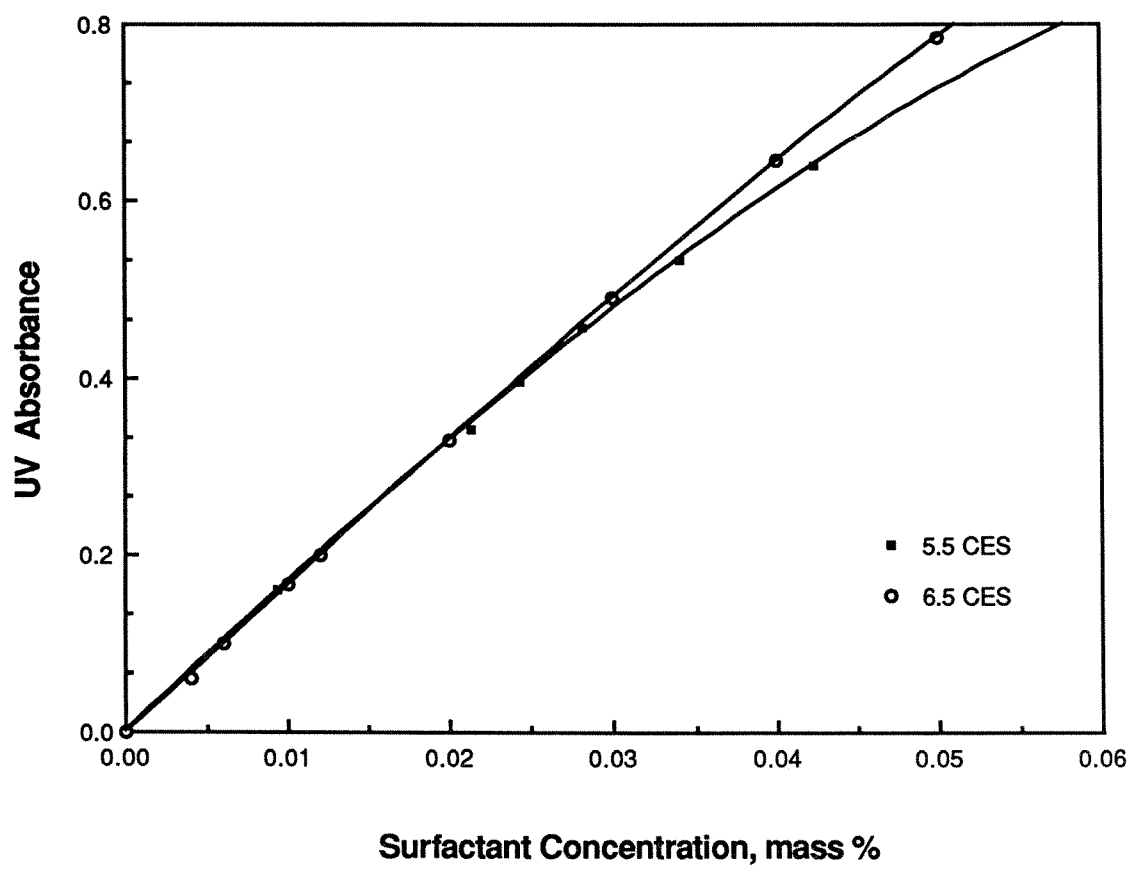


FIGURE 3. - UV absorption vs. concentration of 5.5 and 6.5 CES.

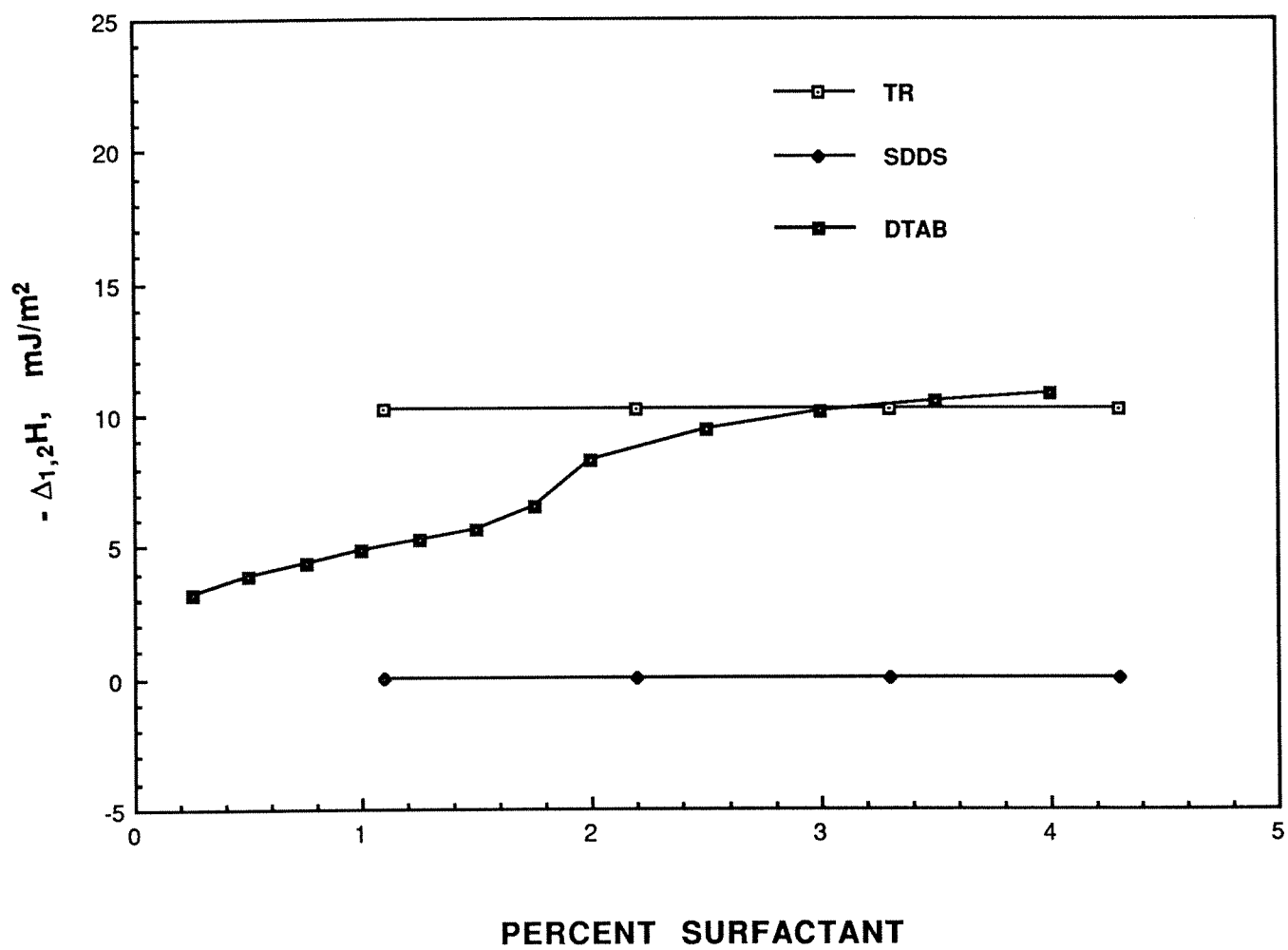


FIGURE 4. - Enthalpy of adsorption of surfactants on SiO₂ at 25° C.

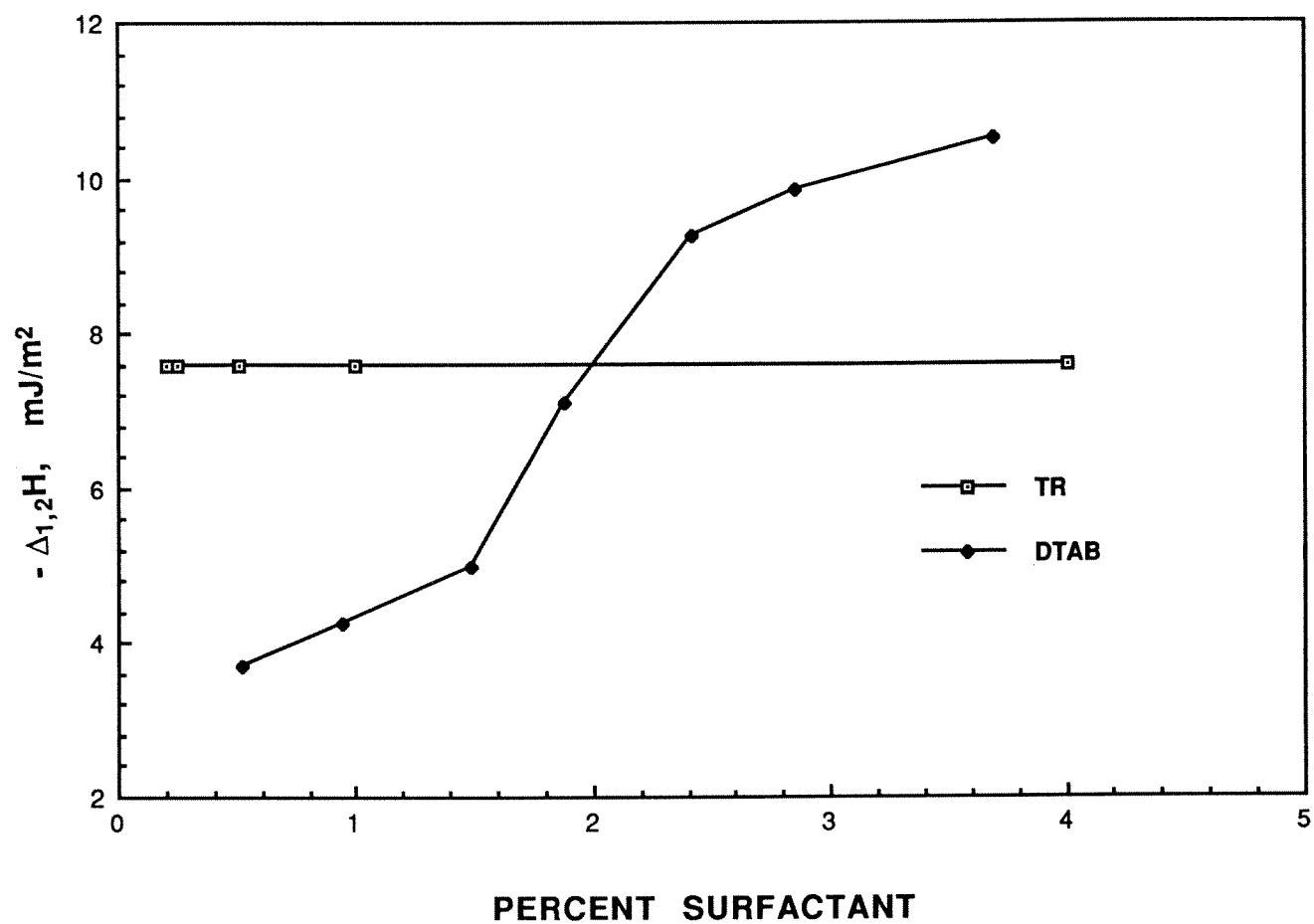


FIGURE 5. - Enthalpy of adsorption of surfactants on SiO_2 at 45°C .

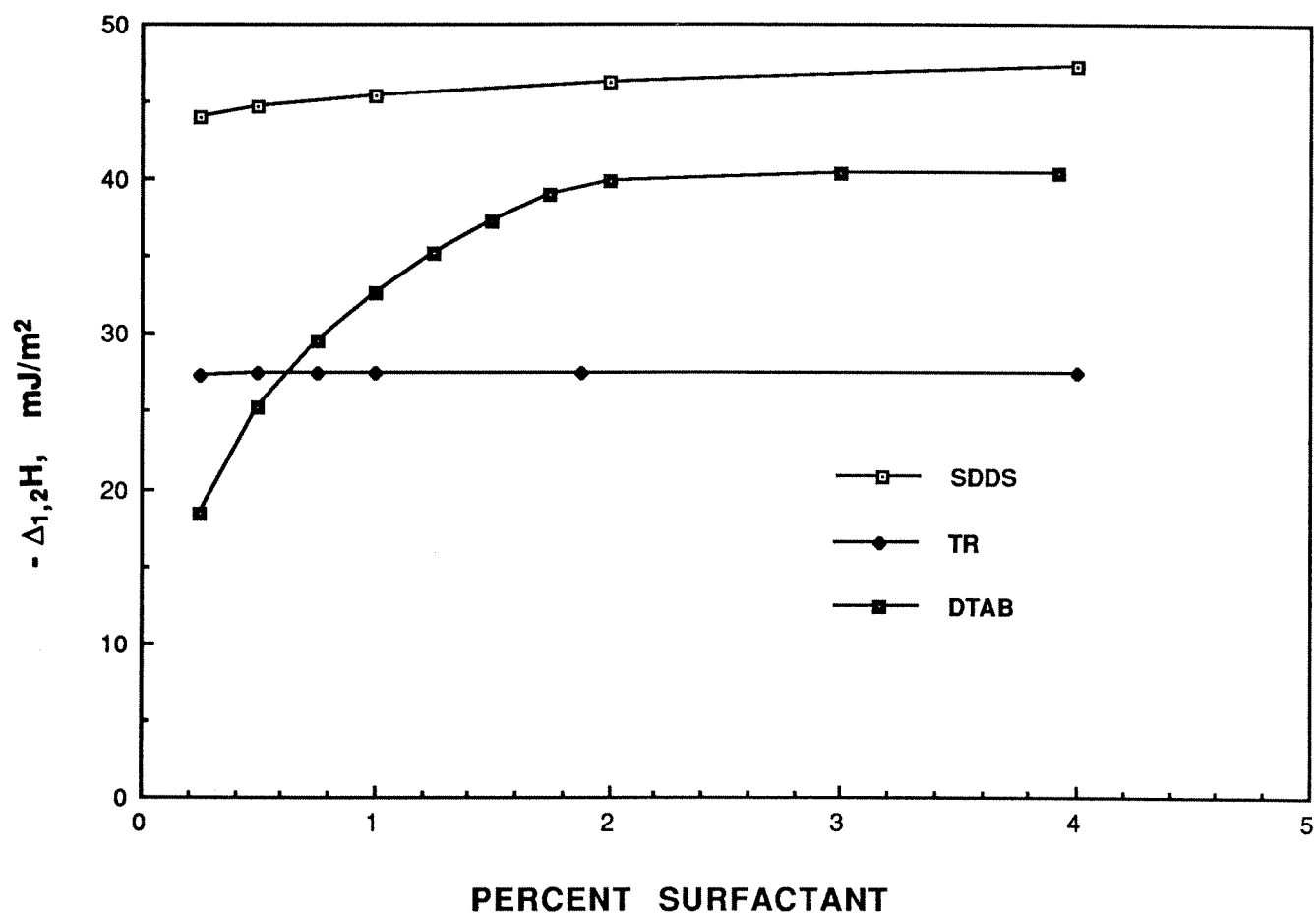


FIGURE 6. - Enthalpy of adsorption of surfactants on $\text{C}_{18}\text{SiO}_2$ at 25°C .

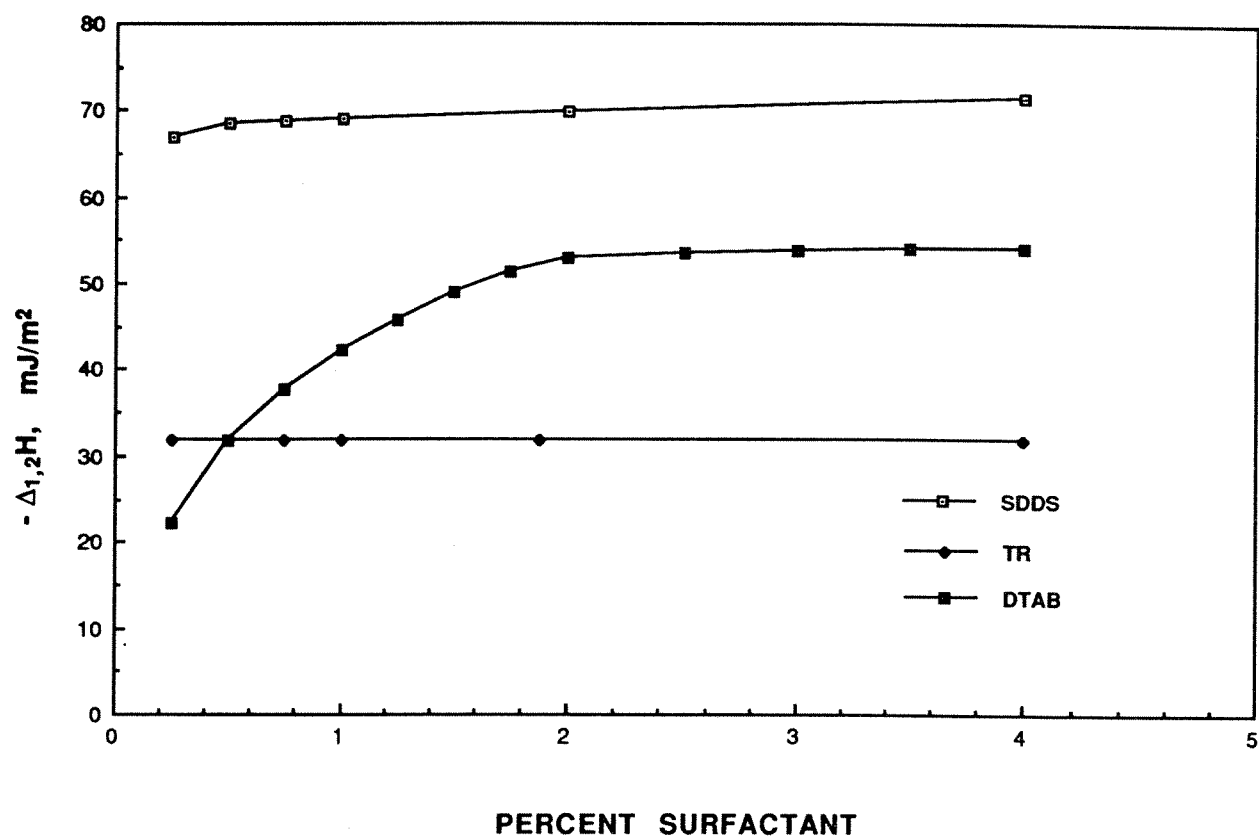


FIGURE 7. - Enthalpy of adsorption of surfactants on C₁₈SiO₂ at 45° C.

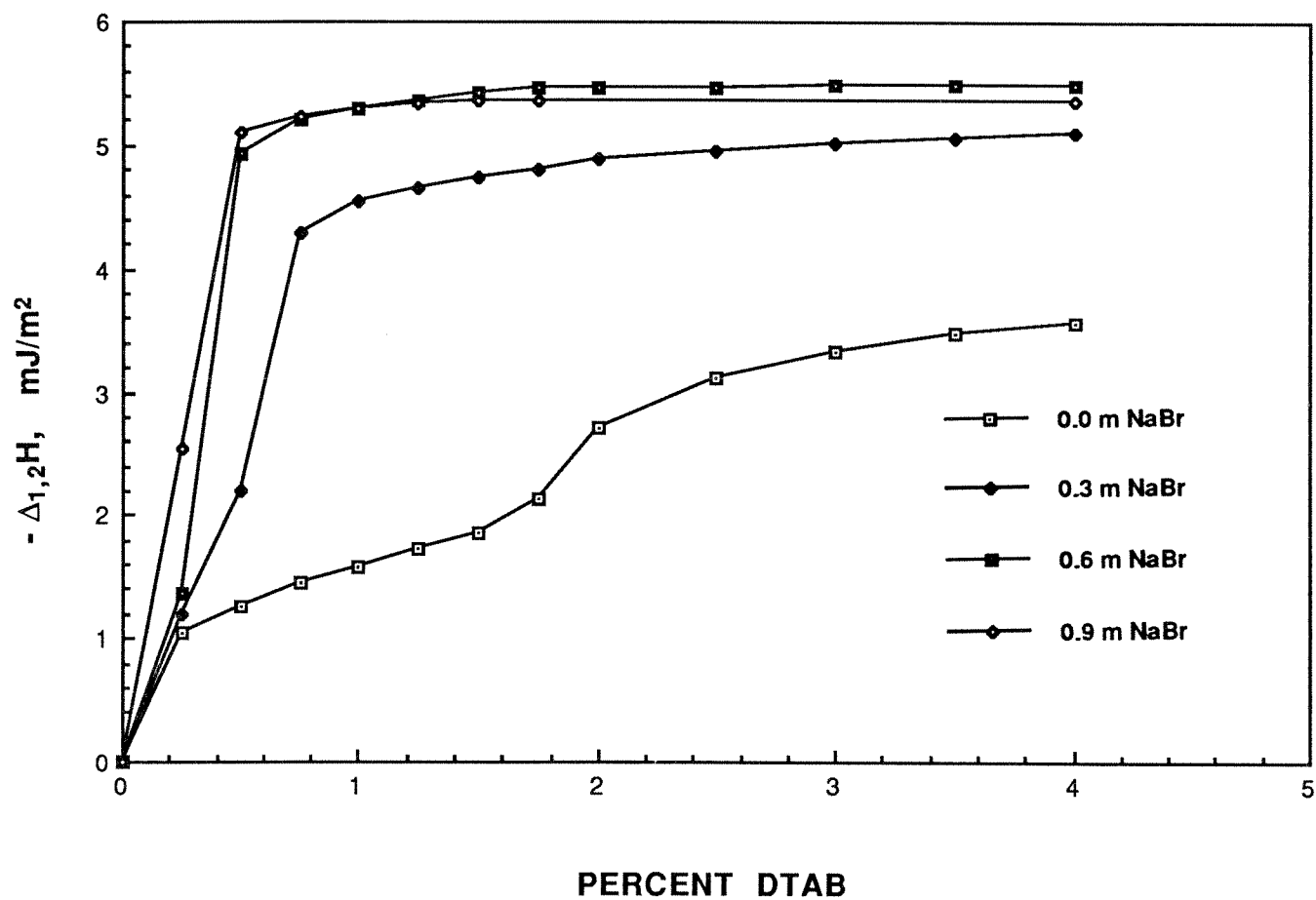


FIGURE 8. - Effect of salinity on the enthalpy of adsorption of DTAB on SiO_2 at 25°C .

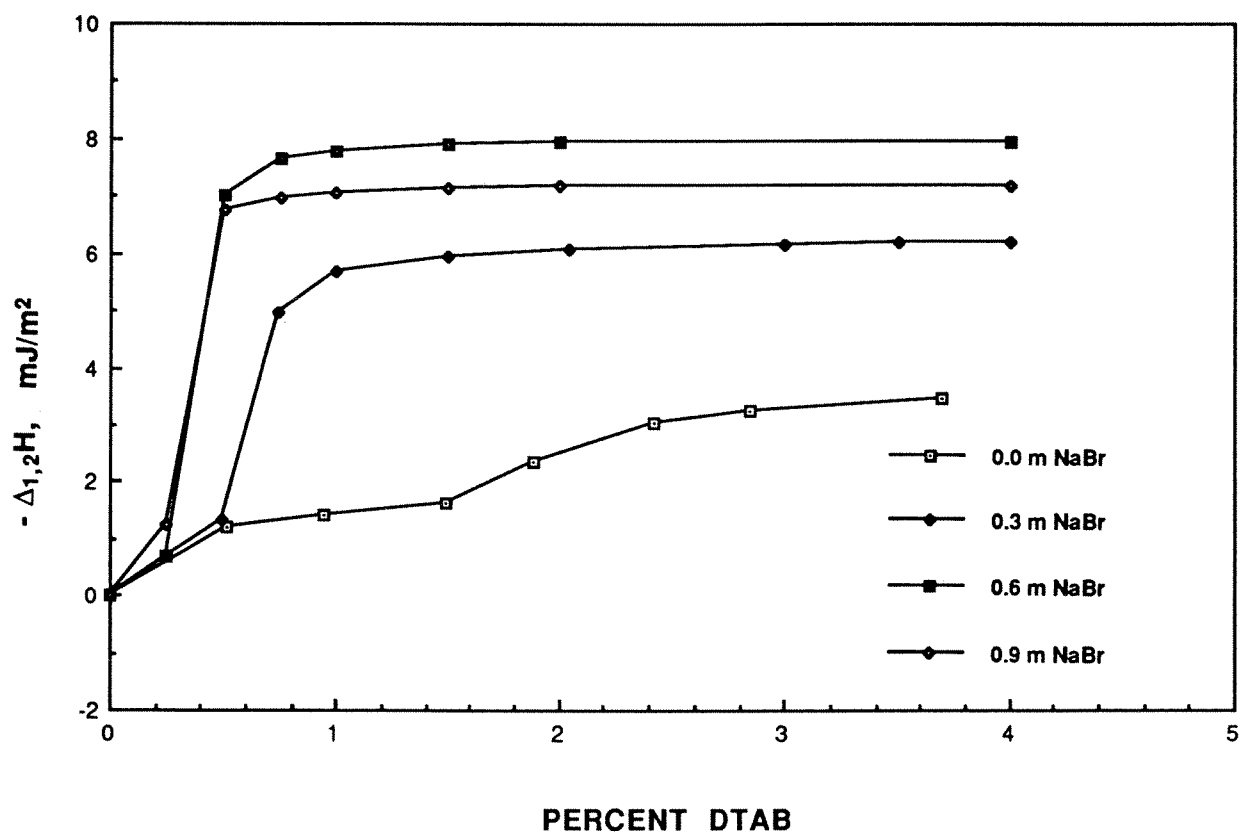


FIGURE 9. - Effect of salinity on the enthalpy of adsorption of DTAB on SiO_2 at 45°C .

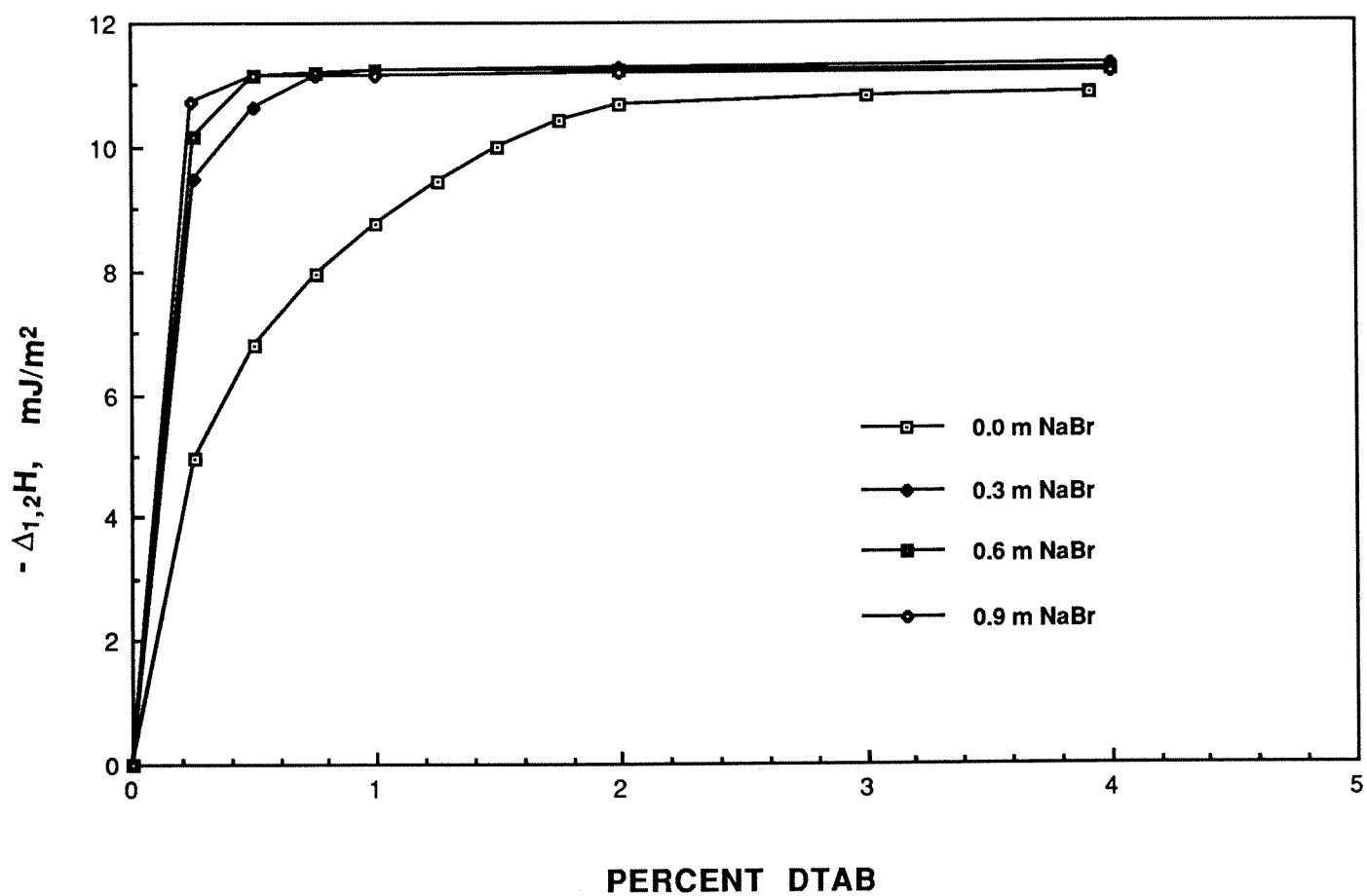


FIGURE 10. - Effect of salinity on the enthalpy of adsorption of DTAB on $C_{18}SiO_2$ at 25° C.

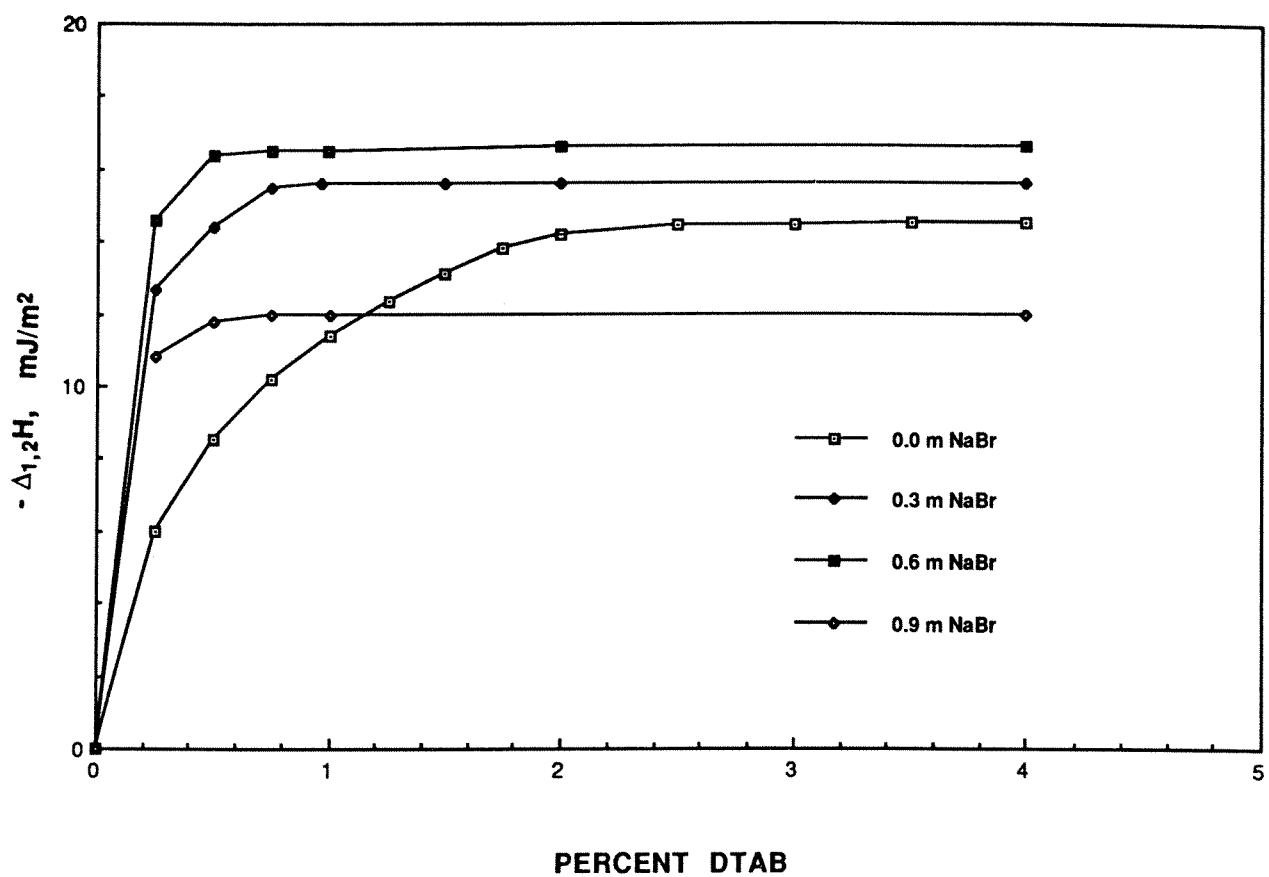


FIGURE 11. - Effect of salinity on the enthalpy of adsorption of DTAB on $C_{18}SiO_2$ at 45° C.

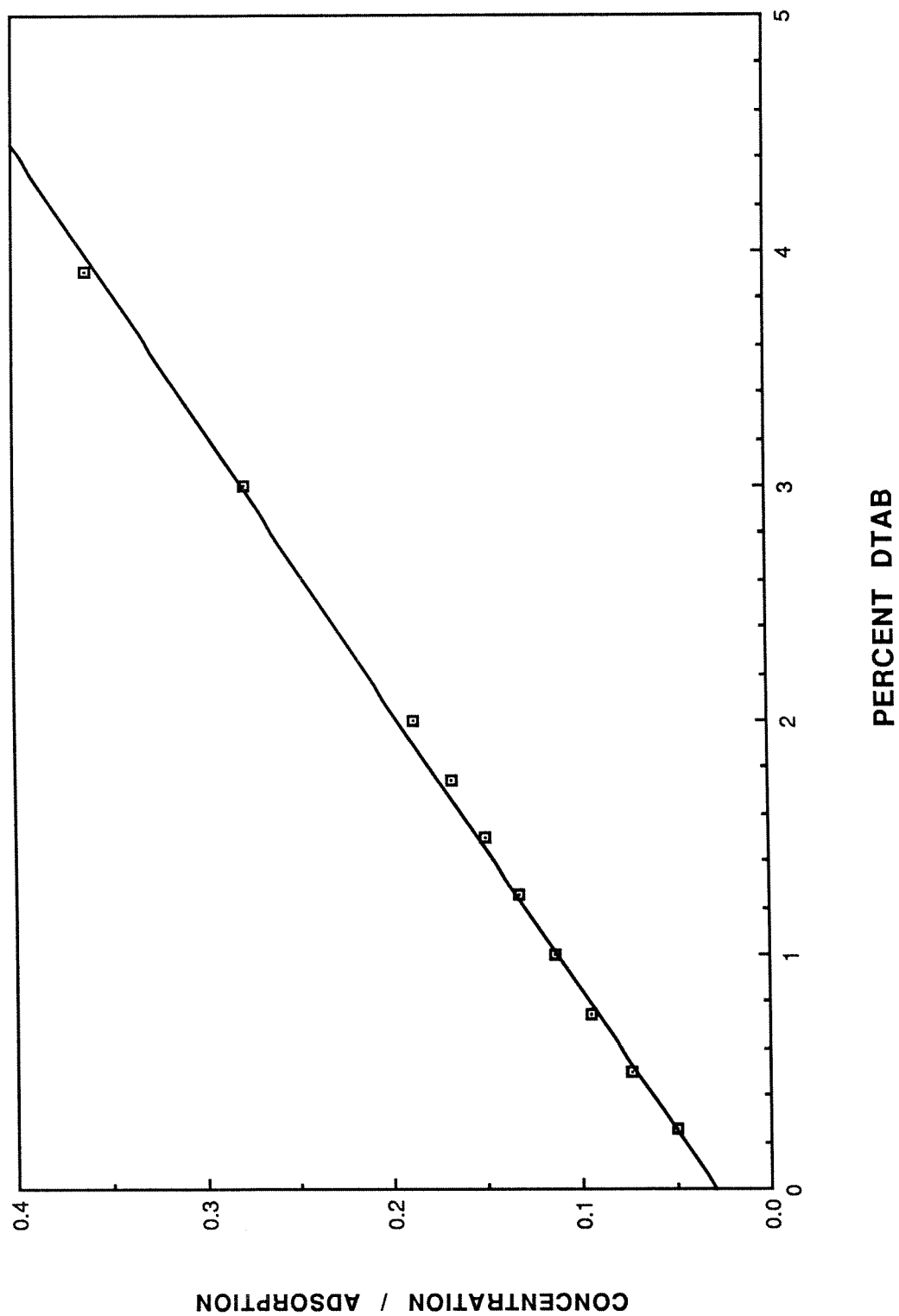


FIGURE 12. - Typical Langmuir plot for DTAB adsorption on $C_{18}SiO_2$, without salt.

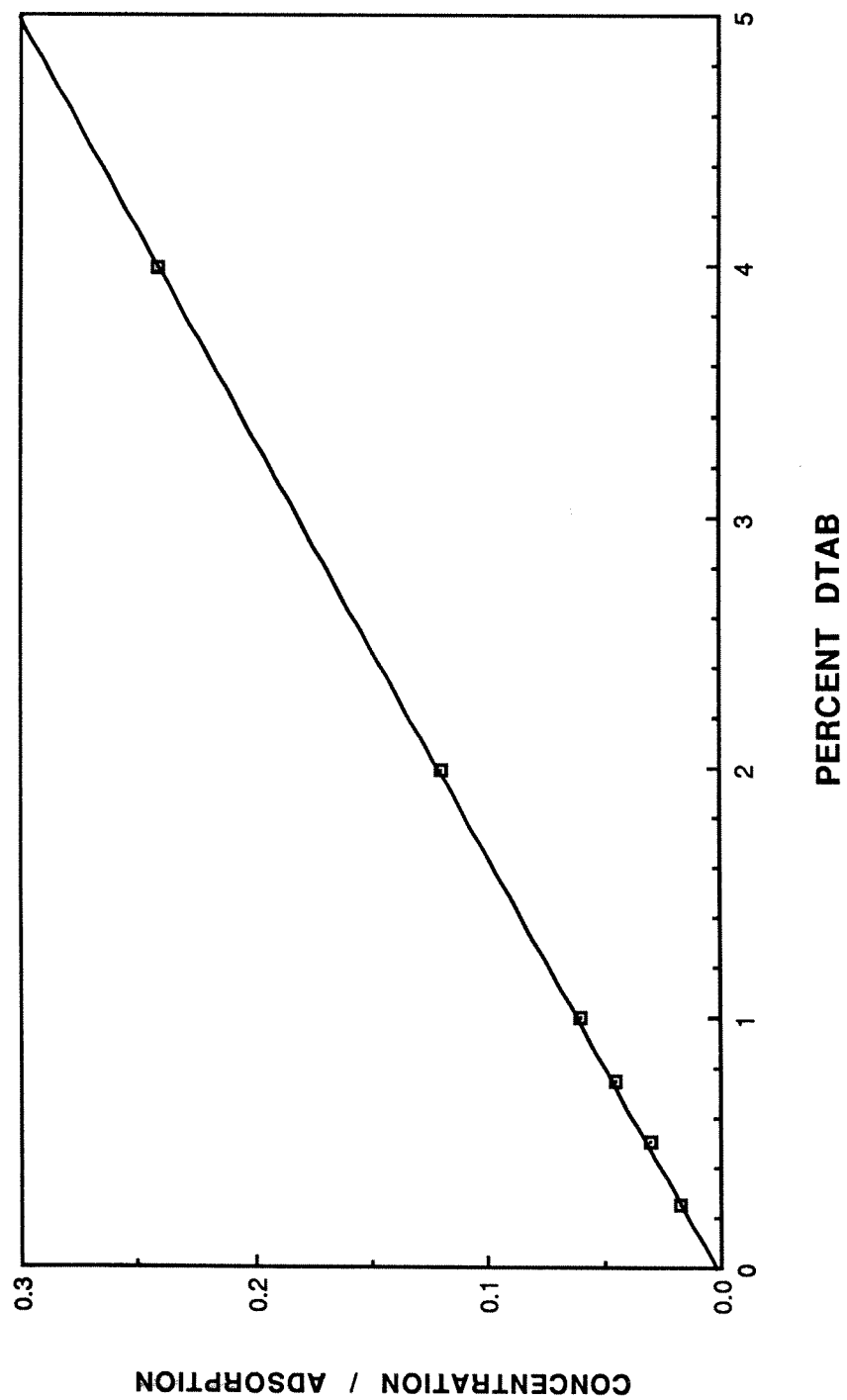


FIGURE 13. - Typical Langmuir plot for DTAB adsorption on C₁₈SiO₂, with salt.

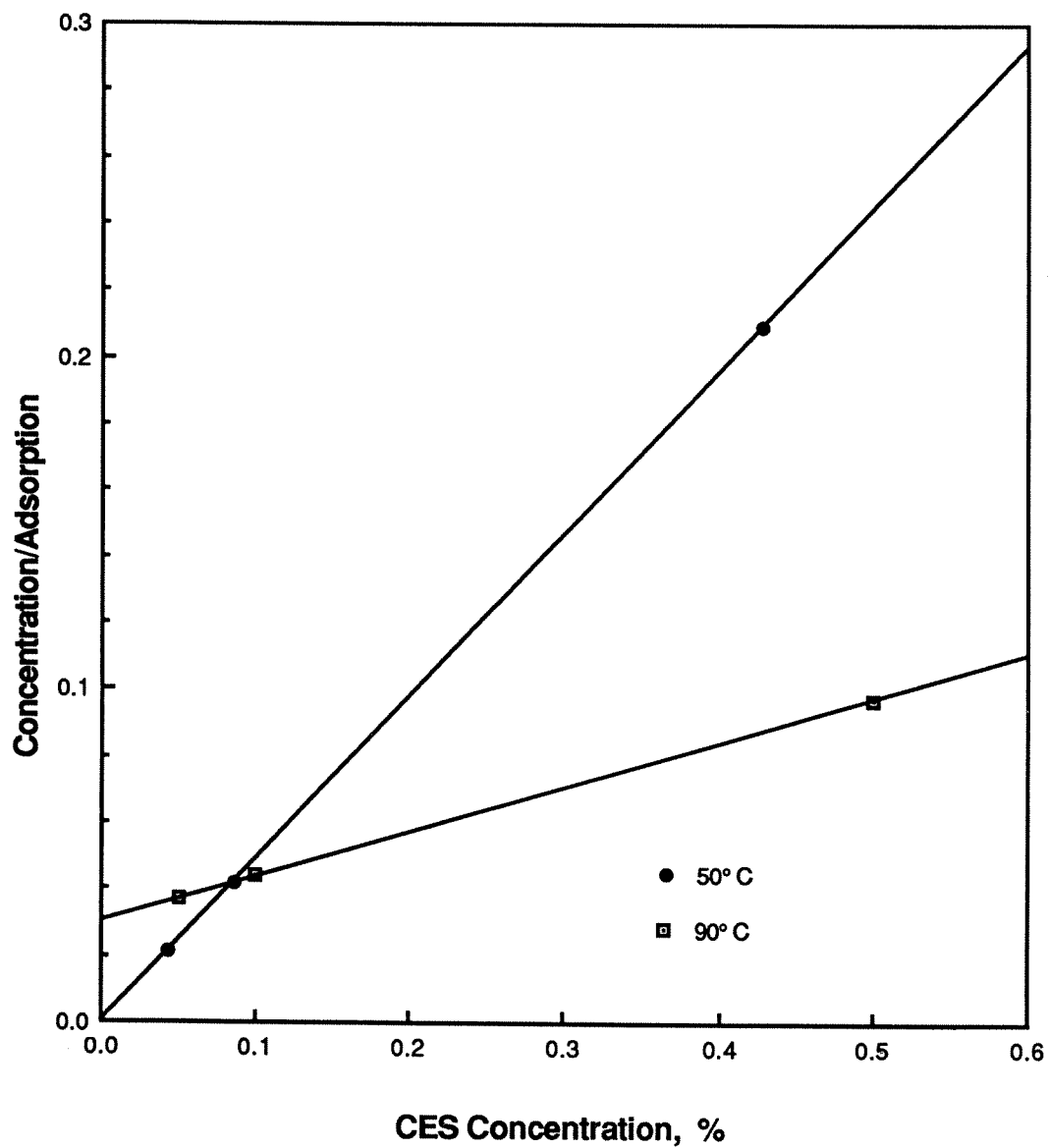


FIGURE 14. - Langmuir plots for 5.5 CES for 50° and 90° C.

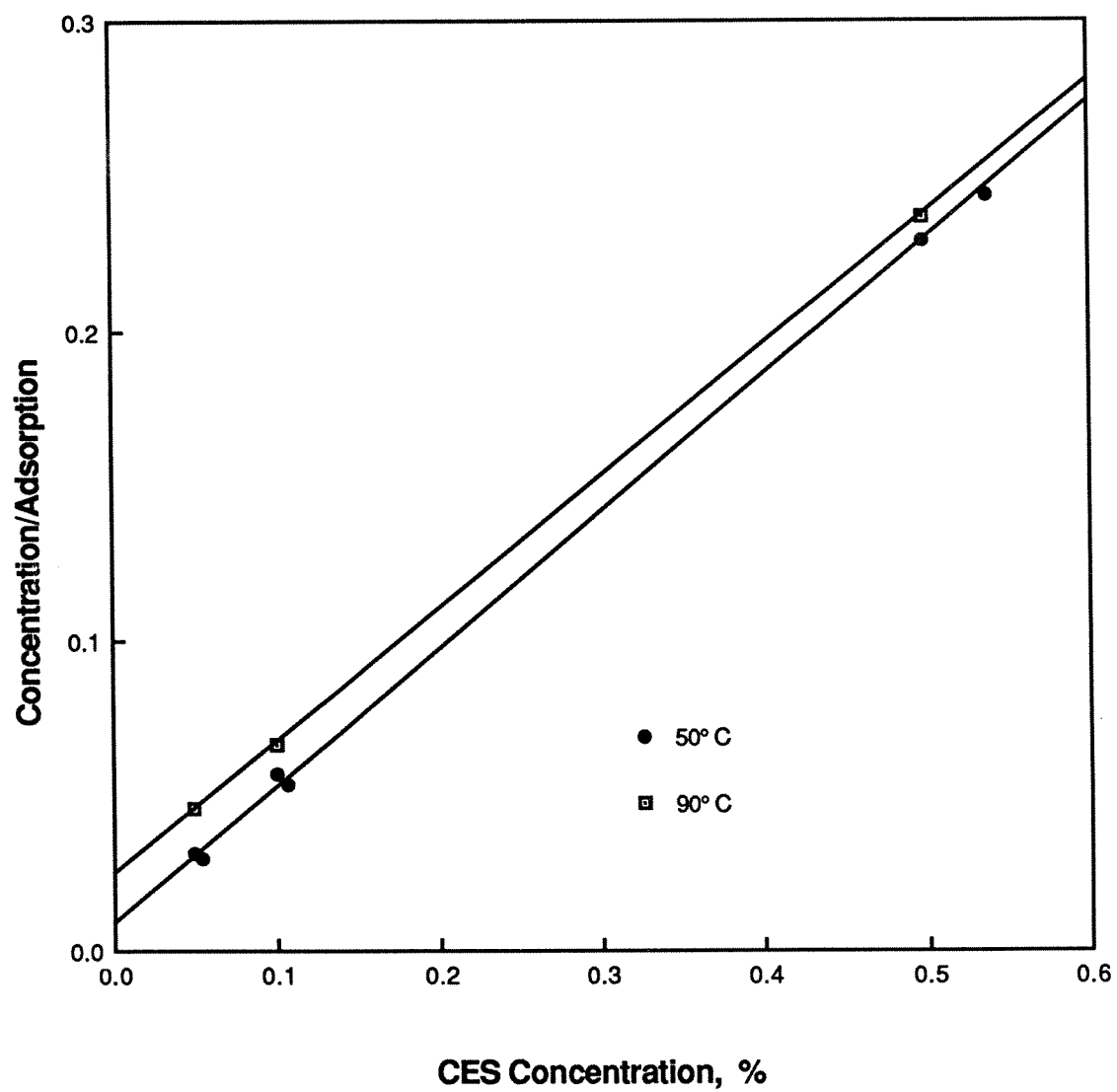


FIGURE 15. - Langmuir plots for 6.5 CES for 50° and 90° C.

